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**ADVANCED AGENT  
IDENTIFICATION AND  
PRELIMINARY ASSESSMENT**



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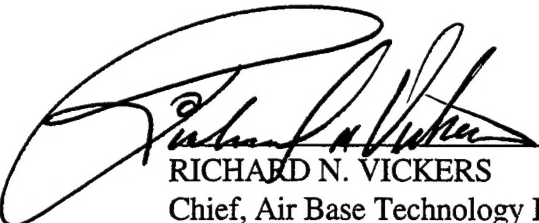
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## LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
ALC	Approximate Lethal Concentration
BP	boiling point
CAA	chemical action agent
CAS	Chemical Abstracts Service
CGET	Center for Global Environmental Technologies
CNS	Central Nervous System
EPA	Environmental Protection Agency
FC	(per)fluorocarbon
FE	(per)fluoroether
GWP	Global Warming Potential
HBFA	hydrobromofluoroamine
HBFE	hydrobromofluoroether
HCFC	hydrochlorofluorocarbon
HFA	hydrofluoroamine
HFC	hydrofluorocarbon
HFE	hydrofluoroether
LFL	Lower Flammability Limit
LOAEL	Lowest Observed Adverse Effect Level
MMT	Methylcyclopentadienyl manganese tricarbonyl
MO	molecular orbital
MP	melting point
NFPA	National Fire Protection Association
NIST	National Institute for Standards and Technology
NMERI	Mexico Engineering Research Institute
NOAEL	No Observed Adverse Effect Level
ODP	Ozone Depletion Potential
PAA	physical action agent
PBB	polybrominated biphenyl
PFC	perfluorocarbon
PFE	perfluoroether
QSAR	Quantitative Structure-Activity Relationship
TMB	trimethoxyboroxine
UFL	Upper Flammability Limit
VB	valence bond

## LIST OF UNITS AND SYMBOLS

b	y intercept for a straight line in an x,y plot
C	Celsius
C <sub>a</sub>	concentration of component a in a gaseous mixture in mole or volume percent
cal	calorie
F	Fahrenheit
f <sub>a</sub>	mole fraction of component a in a mixture
g	gram
J	Joule
k	rate constant for a reaction
K	Kelvin
kcal	kilocalorie
kg	kilogram
kJ	kilojoule
L	liter
LC <sub>Lo</sub>	lowest concentration causing death
LC <sub>50</sub>	concentration required to cause death in 50 percent of an animal test population
LD <sub>50</sub>	dose required to cause death in 50 percent of an animal test population
m	slope of a straight line in an x,y plot
M*	energetically activated third-body molecule
mg	milligram
mL	milliliter
mol	mole
n	normal (straight chain hydrocarbon)
n <sub>D</sub>	refractive index at sodium D line
ppm	parts per million
R	alkyl group (occasionally, also an aryl group)
tert	tertiary
Torr	mm of mercury pressure
X	halogen atom
ΔH	enthalpy change
ΔH <sub>vap</sub>	heat of vaporization
φ	fuel/air equivalence ratio
μm	micrometer (micron, 10 <sup>-6</sup> meter)
•	denotes a free radical, e.g., •H is a hydrogen free radical
*	denotes an energetically activated molecule





## PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET), New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico 87131 for the Advanced Agent Working Group (AAWG) and for the Infrastructure Technology Section of Wright Laboratories (WL/FIVCF), Tyndall Air Force Base, Florida 32403-5319 under Contract F08635-93-C-0073, Task Order 95-04, NMERI Number 8-31183. This document provides the Final Report for the project Advanced Agent Program.

The project Start Date was 16 March 1995, and the End Date was 16 November 1995. The AAWG member organizations are the North Slope Halon Task Group; the U.S. Army - TACOM, the U.S. EPA, Stratospheric Protection Division; Wright Laboratories (WL/FIVCF); and 3M Company. The WL/FIVCF Project Officer is Dr. Charles J. Kibert and the NMERI Principal Investigator is Robert E. Tapscott.

NMERI 1995/15/31883



## EXECUTIVE SUMMARY

### A. OBJECTIVE

The objective of this study is to assess the probability of success and to determine the most promising directions for development of new chemical alternatives to Halon 1301 (bromotrifluoromethane,  $\text{CBrF}_3$ ) in fire suppression and explosion prevention and suppression applications.

### B. BACKGROUND

Halon 1301 and Halon 1211 (bromochlorodifluoromethane,  $\text{CBrClF}_2$ ) are widely used in fire and explosion protection. Halon 1301 is primarily employed in total-flood systems (systems that discharge a gas into a space to suppress any fires contained, to suppress an explosion, or to inert an area against fires and explosions), and Halon 1211 is used primarily in streaming applications (applications where agent is directly discharged onto a fire, usually from a portable extinguisher).

On 31 December 1993, production of halon fire and explosion protection agents was phased out in all developed nations under requirements imposed by the Montreal Protocol, an international treaty. To date, no Halon 1301 substitute has been identified to provide total-flood protection against fires and explosions in normally occupied areas without major changes in system hardware. To lay a foundation for development of such agents requires answers to four questions: (1) What mechanisms are available for chemical action agents (CAAs) for protection against fires and explosions? (2) Based on these mechanisms, what families of chemicals could provide an advanced replacement for Halon 1301? (3) What is the preliminary assessment of manufacturability, global environmental impact, and toxicity for these families? (4) Taking all of the above into account, what are the prospects for a halon replacement for a total flood explosion and fire protection of normally inhabited areas that would allow use without major hardware changes? To answer these four questions, the Advanced Agent Working Group (AAWG), which

is composed of participants from the U.S. Military, from users, and from industry, was established, and a research program was instituted to provide the data.

#### C. SCOPE

A survey of information on explosion protection and fire suppression testing and on mechanisms of chemical protection agents was performed, and the information acquired was assessed to determine directions of future efforts to find chemical substitutes to Halon 1301. Although the present project is oriented toward development of Halon 1301 substitutes, many of the conclusions also apply to Halon 1211 substitutes.

#### D. METHODOLOGY

Relevant information on fire and explosion inertion and on the classes of chemicals was collected and reviewed, and those chemicals or classes of chemicals which showed potential were identified and analyzed. After a review of the data with the AAWG members and other experts, the potential for a Halon 1301 replacement for total-flood applications was assessed.

#### E. APPROACH

Four separate tasks were included in the project:

Task 1: Technology Review and Information System. The initial task was to (1) establish methodologies and software utilities for computerized storage, manipulation, and retrieval of information collected during this project and (2) conduct a detailed search on the mechanisms of explosion and fire inertion and suppression and on families of chemicals.

Task 2: Selection and Grouping of Chemicals and Chemical Families. The information collected was reviewed and it was decided to assess chemicals based on the groups in the periodic table. Each group was assessed individually, and specific compounds within each group which showed potential as a constituent of a Halon 1301 replacement was evaluated separately.

Task 3: Assessment of Potential of Chemicals and Chemical Families. Synthetic and manufacturing procedures for the chemical classes selected and for other chemical classes that may arise were assessed. The toxicity of agents in the chemical families was identified using available toxicity information, using toxicological indices for selected individual related compounds, and, using, where appropriate, Quantitative Structure-Activity Relationships (QSARs). The toxicity assessment was discussed with outside toxicology experts.

Task 4: Determine Prospects for Advanced Halon 1301 Substitutes. The final product is a detailed assessment of the potential for identification and development of advanced agents for total flooding of normally inhabited areas, as reported in this document.

## F. RESULTS

Two large families of compounds have been identified—tropodegradable halocarbons and non-halocarbon candidates. Tropodegradable replacements are highly effective halocarbons that have low atmospheric lifetimes, leading, in most cases, to near-zero global warming and ozone depletion. The most promising nonhalocarbon agents are those containing phosphorus, silicon, and certain transition metals (in particular, iron).

## G. CONCLUSIONS

Non-halocarbon compounds in the phosphorus, silicon, and transition metal families offer promise as candidates for streaming applications (Halon 1211 substitutes) and, to a lesser extent, as total-flood candidates (Halon 1301 replacements). Boron and sulfur compounds could also provide materials for investigation as halon substitutes. The tropodegradable halocarbons offer significant promise as total-flood agents. These compounds include iodocarbons, hydrobromofluoroethers (HBFEs), hydrobromofluoroamines (HBFAs), fluorobromo unsaturated compounds (alkenes and aromatics), and bromofluorocarbonyl compounds. Most of the materials are highly fluorinated (to decrease flammability and hepatotoxicity), but in many cases are not completely fluorinated. These materials appear to have very short atmospheric lifetimes, on the order of days or weeks. Thus the Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are near zero. The major problem is toxicity. The only iodocarbon having a reasonable

toxicity identified to date is trifluoromethyl iodide ( $\text{CF}_3\text{I}$ ), and even this material has too high a toxicity to be considered for total-flood applications in normally occupied areas. Other iodocarbons appear to be more toxic. Note, however, that no information is available on aromatic iodides and these materials may have acceptable toxicities.

The most promising non-halocarbon compounds are the phosphorus compounds (particularly phosphorus nitrides), bromine-substituted silicon and siloxane compounds, and transition metal compounds. A number of these non-halocarbon materials are solids or high boiling point liquids; however, many of these appear to have sufficiently high vapor pressures that they could volatilize completely. Carriers such as hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) may be necessary in some cases. Of particular interest are the phosphorus nitrides. Preliminary work on these materials shows them to have extinguishment concentrations much less than those of the halons.

#### H. RECOMMENDATIONS

Work should continue with an emphasis on those compounds identified above. The phosphorus nitrides, silicon compounds, metal compounds, and tropodegradable halocarbons are the most promising. The latter compounds are the most promising for total-flood applications.

## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The objective of this study is to assess the probability of success and to determine the most promising directions for development of new chemical alternatives to Halon 1301 (bromotrifluoromethane,  $\text{CBrF}_3$ ) in fire suppression and explosion prevention and suppression applications.

#### B. BACKGROUND

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To answer these four questions, the Advanced Agent Working Group (AAWG)—composed of participants from the U.S. Military, from users, and from industry—was established. Once answers to these questions are in hand, an intelligent decision can be made about the direction of future initiatives and about those chemicals most likely to provide an answer.

There is danger in setting criteria for agents that are too narrow or that may change in view of future regulatory activities. However, any Halon 1301 replacement agent for use in normally occupied areas with minimal retrofit should meet the following criteria: (1) The agent must provide three-dimensional protection against fires and explosions. Note that this is not the same as “cleanliness,” although it is related. (2) The agent must have an effectiveness essentially equivalent to Halon 1301. Here “equivalent” does not mean “identical.” The target is for an agent that does not require significant redesign of the delivery system. (3) The agent must have a near-zero Ozone Depletion Potential (ODP), Global Warming Potential (GWP), and atmospheric lifetime. It would be inappropriate to set numbers, since historically numbers have changed. But the ODP must be very low, if not zero. Similarly, the atmospheric lifetime must be very low, certainly on the order of a few years, at most; a more desirable lifetime would be weeks or days. (4) The agent must be applicable to normally occupied areas. Practically, under the present National Fire Protection Association (NFPA) Standard on Clean Agent Fire Extinguishing Systems (Reference 1), this means that the agent must have a design concentration lower than the No Observed Adverse Effect Level (NOAEL) value, regardless of what the NOAEL is based on.\* An excellent and thorough overview of regulatory, toxicological, and other criteria for options to the use of halons can be found in Reference 2.

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\*An exception allows the use of a halocarbon agent up to the Lowest Observed Adverse Effect Level (LOAEL) for Class B hazards in normally occupied areas where a predischARGE alarm and time delay are provided. The time delay must be set to ensure that occupants have time to evacuate prior to the time of discharge.

## C. APPROACH

To answer the four questions posed above, four tasks were developed:

Task 1: Technology Review and Information System: The initial task was to establish methodologies and software utilities for computerized storage, manipulation, and retrieval of information collected during this project. A detailed search strategy on the mechanisms of explosion and fire inertion and suppression was of primary interest during a library search for relevant data.

Task 2: Selection and Grouping of Chemicals and Chemical Families: The information collected was reviewed, chemicals were assess by periodic table group. Each group was assessed individually, and specific members of each group which showed potential as a constituent of a Halon 1301 replacement was evaluated separately.

Task 3: Assessment of Potential of Chemicals and Chemical Families: Synthetic and manufacturing procedures for the chemical classes selected were assessed. The toxicity of agents in the chemical families were identified using available toxicity information and toxicological indices for selected individual related compounds. The toxicity assessment was discussed with outside toxicology experts.

Task 4: Determine Prospects for Advanced Halon 1301 Substitutes: The final product is a detailed assessment of the potential for identification and development of advanced agents for total flooding of normally inhabited areas, as reported in this document.

## SECTION II

### DATA COLLECTION AND STORAGE

Physical action agents (PAAs) are those that operate primarily by heat absorption. Chemical action agents (CAAs) are those that operate primarily by chemical means—removal of flame free radicals. In general PAAs are more effective than CAAs. The first question to be answered is “What mechanisms are available for CAAs for protection against fires and explosions?” A survey of all information on explosion protection and fire suppression testing and on mechanisms of chemical protection agents was performed. While most of the data needed had already been collected in efforts at the New Mexico Engineering Research Institute (NMERI), primarily under Air Force and Environmental Protection Agency (EPA) sponsorship, and by the National Institute for Standards and Technology (NIST), the data have not been thoroughly analyzed for development of a total-flood agent for normally occupied areas.

A database, the “Advanced Agent Database,” was develop to store and compile information on potential fire extinguishing agents and chemical reaction information related to fire extinguishment and explosion protection. The Advanced Agent Database is linked to the larger NMERI Library Database, which contains 4000 references on ozone depleting chemicals and fire extinguishment mechanisms, for citation and abstract data. The Advanced Agent Reference Database also includes pages on which conclusions as to the applicability of each document can be entered, and concepts, which the concepts of potential use are displayed. The database is documented in a separate report (Reference 3). Many of the references in the body of this report have been included in the database; however, in many cases, references to patents and to general reviews have been omitted.

Under sponsorship of the Stratospheric Ozone Protection Division of the EPA, a previously existing database of halocarbon chemicals that could be considered as potential substitutes for halons was modified, expanded, and checked (References 4 and 5). The CGET/EPA CHEMICAL Database (called the CHEMICAL Database) provides readily accessible physical, chemical, and toxicity data on over 900 chemical compounds being

considered or commercialized as replacements for ozone depleting substances (ODSs). While most of the compounds are halocarbons and contain halogens (chlorine, fluorine, bromine, and/or iodine), others are non-halogens. Most of these are compounds of phosphorus, nitrogen, silicon, sulfur, and oxygen. The database was established to assist developing replacements for ODSs with the present emphasis on fire protection. The properties section contains environmental, solubility, inhalation toxicity and exposure limits, physical property, thermodynamic, and extinguishment and flammability data. For a limited number of compounds, drawings of the chemical structure are provided. The toxicity section contains results from animal species testing for selected compounds.

### SECTION III

#### FIRE AND SUPPRESSION

##### A. FIRE DYNAMICS

Fires are highly complex, inhomogeneous, and involve both mass and energy transport. To some extent, the inhomogeneity and the complexity can be reduced using flames, in particular, premixed air/gas flames. On the other hand, diffusion flames (Figure 1) are more representative of real fires.

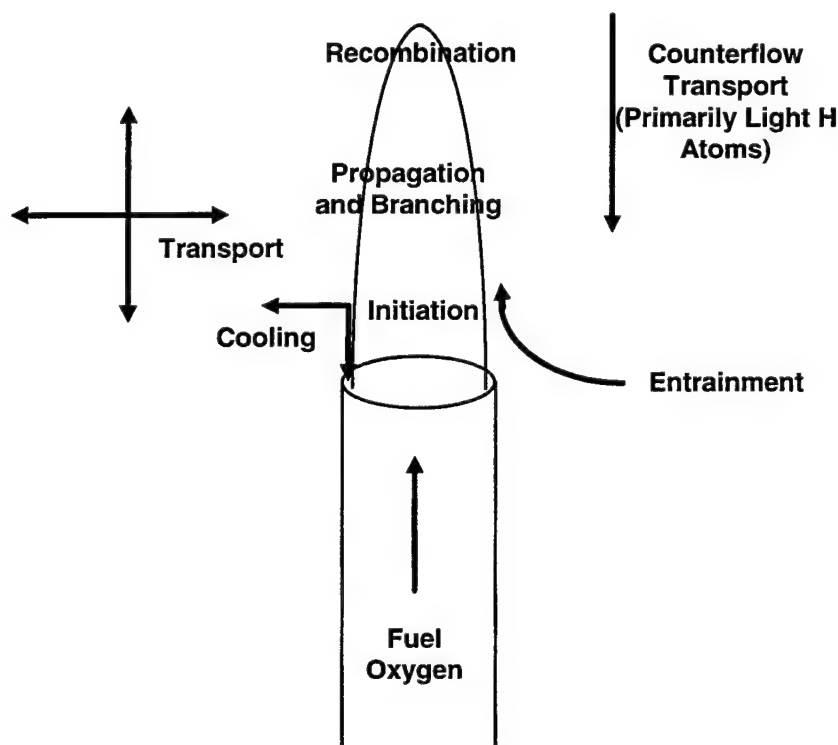


Figure 1. Diffusion Flame.

One of the authors (Brabson) has examined the flicker rate for flat flames with inert gas sheathes and has seen two frequencies. The lower frequency seems to be due to the interaction of the flame with the sheath gas, and presents an opportunity to study the entrainment of extinguishants in a burner flame as a function of fuel/air equivalence ratio ( $\Phi$ ). This frequency

changes as the flow rate of the sheath gas (nitrogen) is changed. The higher frequency is thought to be due to interactions within the flame. Upon addition of extinguishant, the flicker rate changes by about a factor of 3 as one proceeds from extinguishant to flameout. To separate these two frequencies, the digitized data have been submitted to Fourier analysis. Instead of getting two frequencies, one observes a fundamental and several overtones. If one can isolate a second (higher) frequency, this could provide a new tool for characterizing the progress toward extinguishment. Moreover, since a single data point requires a 1-second measurement, one could completely characterize an extinguishant, both as a function of amount of extinguishant added and as a function of  $\Phi$ , in a few hours and obtain a very complete profile of the flame-extinguishant interaction.

## B. PHYSICAL AND CHEMICAL SUPPRESSION

### 1. Physical and Chemical Mechanisms

Fire suppression by chemical agents occurs through two mechanisms—physical and chemical (Reference 6). Physical mechanisms include heat absorption and dilution. Chemical mechanisms involve actual disruption of the chemical processes that maintain combustion. It is important to note that the two effects often occur together. In some cases (e.g., extinguishment with nitrogen), physical suppression can occur without any significant contribution by a chemical mechanism, although, even here, one can postulate chemical mechanisms such as free-radical recombination effected by use of nitrogen molecules as third bodies to remove excess energy (see, e.g., Reaction 1, where  $N_2^*$  represents an energetically activated nitrogen molecule).<sup>\*</sup> On the other hand, chemical suppression must always be accompanied by physical suppression since all chemical agents have the ability to absorb heat and to effect dilution.



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<sup>\*</sup>Throughout this report, equation numbers are inserted in brackets, [], and chemical reaction numbers are placed in parentheses, ().

For most scenarios, the primary physical suppression mechanism is heat absorption. Using a method proposed by Sheinson (Reference 6), it can be shown that the extinguishing concentrations of most halocarbon agents that do not contain bromine (or iodine) is determined well by heat absorption (Reference 7). This is the primary reason that extinguishment concentrations usually decrease with increasing molecular weight (increasing vibrational modes for heat absorption). This effect can be seen in Figure 2, where the cup burner extinguishment concentrations for a series of linear perfluorocarbons are plotted as a function of the number of carbon atoms using data from the 5/8-scale NMERI cup burner (Reference 8).<sup>\*</sup> Others have shown that extinguishment by all agents is dominated by heat absorption, and that many of the effects attributed to chemical mechanisms may be thermodynamic rather than kinetic (Reference 9), conclusions not accepted by many researchers.

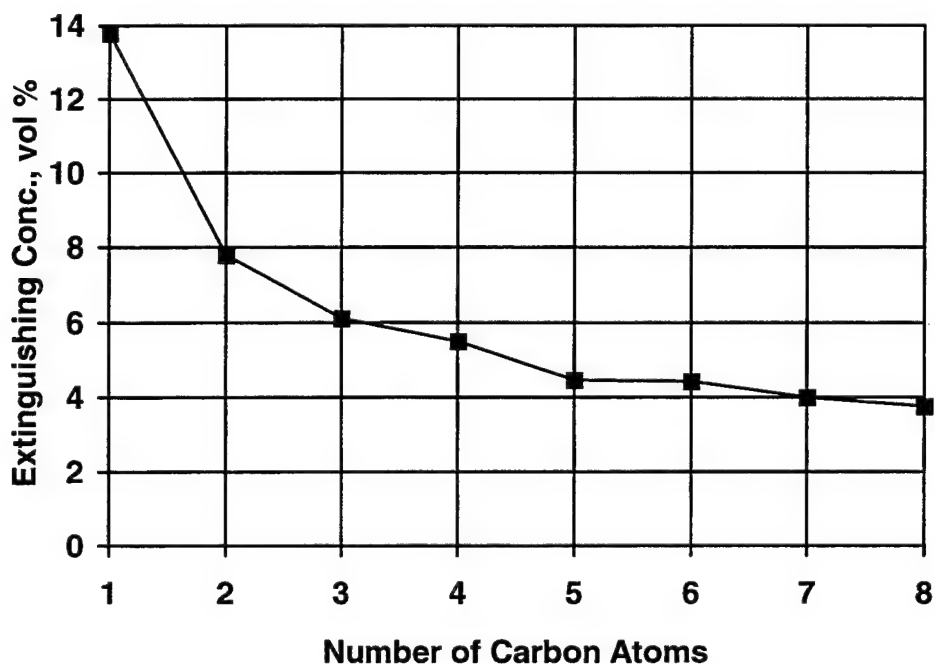
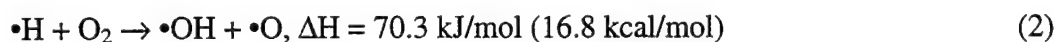


Figure 2. *n*-Heptane Cup-Burner Extinguishment Concentrations for Linear Perfluorocarbons.

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<sup>\*</sup>An erroneous value of 12 percent for perfluoropentane is reported in the cited paper. A redetermined value of 4.45 percent is used here.

The primary mechanisms for chemical inhibition of hydrocarbon flames are believed to be removal of highly reactive free radicals that maintain combustion—hydrogen atoms ( $\bullet\text{H}$ ), hydroxyl free radicals ( $\bullet\text{OH}$ ), and oxygen atoms ( $\bullet\text{O}$ ). Based on the relative abundance of these three species and their importance in driving combustion, it is generally believed that hydrogen-atom removal is the most effective inhibition pathway, followed by removal of hydroxyl free radicals, and finally removal of oxygen atoms. The relative importance of these three processes is still debated, however, and may depend on the fuel and flame characteristics. Removal of hydrogen atoms has a large effect owing to the relatively high abundance of these species in a fire. Hydrogen plays an important role in the primary chain-branching reaction that sustains combustion of hydrocarbon fuels (Reaction 2, Reference 10). It must be noted that equilibrium between the major combustion free radicals ( $\bullet\text{H}$ ,  $\bullet\text{OH}$ ,  $\bullet\text{O}$ ) is achieved rapidly so that it makes little difference which free radical is removed in effecting suppression.



Two methods have been proposed to determine the physical and chemical contributions of an agent to extinguishment. These are discussed below.

## 2. The Method of Sheinson as Modified by Fernandez

Sheinson and Driscoll (Reference 11) and Sheinson, Penner-Hahn, and Indritz (Reference 6) have presented a method to quantify suppression action pathways for each of the substituents in an extinguishing agent.\* A subsequent paper has refined and expanded the models (Reference 12). Dr. Richard E. Fernandez has taken Sheinson's method and recast the calculation method in a slightly different form.

The flame-spread rate for burning material is a strong inverse function of the heat capacity per mole of oxygen of the oxidizing atmosphere. As a result, if the heat capacity of an atmosphere is raised to approximately 40 to 50 cal/mol-°C per mole of  $\text{O}_2$  present (209 J/mol-K

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\*Fernandez, R. E. , "Commercially Available Halon Replacements and Their Manufacture," Committee on Fire Suppression Substitutes and Alternatives, National Research Council, National Academy of Science, San Diego, California, 14-16 August 1996. (Unpublished)



per mole of O<sub>2</sub>), combustion is not supported (References 13 and 14). This criterion can be used to calculate the concentration of a given agent required to suppress a fire by heat absorption only. The difference between the calculated and actual concentrations can then be attributed to suppression mechanisms other than purely physical (i.e., chemical suppression).

When a total-flooding agent is discharged into an enclosed volume and the pressure is maintained constant by leakage, the oxygen concentration decreases. Regardless of the agent used, the O<sub>2</sub> concentration (C<sub>O2</sub>) and the agent concentration (C<sub>a</sub>), both in mole or volume percent, are related by Equation 1. This equation assumes ambient air containing 21 volume percent O<sub>2</sub> (i.e., before addition of agent, C<sub>O2</sub> = 21 percent).

$$C_a = -4.7619(C_{O_2}) + 100 \quad [1]$$

Three calculations are required to determine the agent concentration, C<sub>a</sub>, required to raise the total heat capacity of an enclosed area to 50 cal/mol-°C/mole of O<sub>2</sub>.<sup>\*</sup> (1) The mole (or volume)<sup>†</sup> percent of agent required to impart to air a heat capacity of 50 cal/mol-°C/mole of O<sub>2</sub> at 25 °C and constant pressure while maintaining a constant oxygen concentration (e.g., 20 mole percent) is calculated. In other words, the oxygen concentration is held constant at 20 mole percent and the nitrogen/argon (N<sub>2</sub>/Ar) concentration is decreased as agent is added. (2) A second calculation is made assuming a different constant O<sub>2</sub> concentration (e.g., 16 mole percent). 3. These data are then used to calculate, for each agent, the equation of the line that represents an atmosphere where combustion cannot be sustained because the heat capacity is 50 cal/mol-°C/mole of O<sub>2</sub>. A sample calculation is given below for HFC-125 (pentafluoroethane, CHF<sub>2</sub>CF<sub>3</sub>).<sup>‡</sup>

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<sup>\*</sup>The value of 50 cal/mol is probably high (45 cal/mol may be a better estimation). This will tend to make the chemical contributions a little higher than they should be. Though the specific heat capacity assumed will affect the concentrations calculated, it will not affect the rank ordering of agents based on the apparent chemical contribution to extinguishment.

<sup>†</sup>For mixtures of ideal gases, mole and volume percent are identical and the terms are used interchangeably throughout this report.

<sup>‡</sup>A definition of halocarbon numbers, such as HCFC-123, can be found in *Halocarbon Nomenclature*, CGET3, Center for Global Environmental Technologies, University of New Mexico, Albuquerque, New Mexico, February 1996, which is available upon request.

At 25 °C and 1 atmosphere pressure, the vapor-phase heat capacity of HFC-125 is 22.93 cal/mol °C (800 J/kg-K, Reference 1). Under normal conditions, the composition of ambient air is approximately 21 mole percent oxygen, 78 mole percent nitrogen, and 1 mole percent argon. The heat capacity of oxygen (O<sub>2</sub>) is 7.016 cal/mol °C (29.37 J/mol K), that of nitrogen (N<sub>2</sub>) is 6.961 cal/mol °C (29.15 J/mol K), and that of argon (Ar) is 4.9679 cal/mol °C (20.800 J/mol K) (Reference 15). The average heat capacity of N<sub>2</sub>/Ar in the ratio found in air (78 percent/1 percent) is calculated as 6.936 cal/mol °C (29.04 J/mol K). Thus, the heat capacity of a mixture of HFC-125, O<sub>2</sub>, and N<sub>2</sub>/Ar is given by  $f_{125}(22.933) + f_{O_2}(7.016) + f_{N_2/Ar}(6.9528)$  cal/mol °C, where  $f_a$  is the mole fraction of component a. This must be set equal to the heat capacity of 50 calories/mole-K/mole of O<sub>2</sub>. Thus for 1 mole of mixture,  $f_{125}(22.933) + f_{O_2}(7.016) + f_{N_2/Ar}(6.9528) = 50f_{O_2}$ . If  $f_{O_2}$  is maintained at 0.20, this becomes

$$f_{125}(22.933) + 0.20(7.016) + (1-0.20-f_{125})(6.9528) = 50(0.20) \quad [2]$$

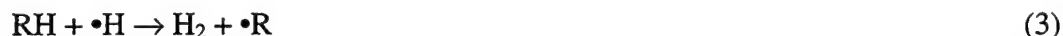
Solving Equation 2 gives  $f_{125} = 0.1905$  (19.05 mole percent). The same procedure for an oxygen concentration of 16 mole percent gives  $f_{125} = 0.0657$  (6.57 mole percent).

The relation between the HFC-125 and O<sub>2</sub> concentrations ( $C_{125}$  and  $C_{O_2}$ ) is linear and can be written in the form  $y = mx + b$ , where  $y$  is  $C_{125}$ ,  $x$  is  $C_{O_2}$ ,  $m$  is the slope of the line, and  $b$  is the y intercept. The two (x, y) data pairs calculated earlier are (20, 19.05) and (16, 6.57). The slope is given by  $m = (19.05-6.57)/(20-16) = 3.12$  and the y-intercept is  $b = 6.57 - (3.12)(16) = -43.36$ . Thus, the equation relating the concentration of HFC-125 to the concentration of O<sub>2</sub> for an atmosphere that will not support combustion due to its heat capacity is

$$C_{125} = 3.12(C_{O_2}) - 43.36 \quad [3]$$

This line defines a family of mixtures containing HFC-125, O<sub>2</sub>, and N<sub>2</sub>/Ar. Only one mixture on this line can be formed by discharging HFC-125 into an enclosed volume. That unique mixture is the intersect of the HFC-125 line described by Equation 3 and the oxygen depletion line defined by Equation 1 with  $C_a = C_{125}$ . The intersection of these two lines is found by solving the simultaneous Equations 1 and 3. For HFC-125, this gives  $C_{O_2} = 18.19$  mole percent and  $C_{125} = 13.39$  mole percent.

For a series of halocarbons, Table 1 gives concentrations calculated by the method described above, observed concentrations, and ratios of the calculated and observed concentrations.\* The observed concentrations were determined with the 5/8-scale NMERI cup burner (Reference 8). The vapor-phase heat capacities are from a variety of sources and were taken from the CGET/EPA Chemical Options Database (References 4 and 5).† For the most part, the agents with the largest chemical contributions to extinguishment contain bromine or iodine, as expected. The large apparent chemical contributions to HCC-280fa ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ ) and HCC-280da ( $\text{CH}_3\text{CHClCH}_3$ ) appears surprising; however, these materials are actually flammable and the relatively low cup burner extinguishment concentrations are almost certainly due to exceeding the upper flammability limit. Another way of looking at this is that the hydrogen atoms in these agents are serving to remove free radicals (e.g., Reaction 3). A number of other observations (e.g., the apparently large chemical contributions to extinguishment by CFCs and by HFC-23 [ $\text{CHF}_3$ ,  $\text{HFCF-22}(\text{CHClF}_2)$ ], and some others) are noteworthy; however, interpretation of these is reserved for the future.



### 3. The Experimental Method of Brabson

Brabson and coworkers have developed a technique to characterize extinguishment for the contribution from physical and chemical mechanisms and to determine the extinguishment end point by measuring heat removal using a flat-flame burner (References 16 and 17).‡ This is similar to the method of Botha and Spalding for determination of the adiabatic flame speed by relating the observed flame speed to the heat removed by a burner as the mixture ratio was changed (Reference 18). Pre-mixed methane-oxygen-argon flames are

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\*The numbers of significant figures in this table are admittedly higher than is probably justified.

†Contact the Center for Global Environmental Technologies at the University of New Mexico for information on this database.

‡Brabson, G. D., Schiro, J., Patterson, R. A., Walters, E. A., and Tapscott, R. E., "Determination of Extinguishment Mechanisms," International CFC and Halon Alternatives Conference, Washington, DC, USA, 23-25 October, 1995. (Unpublished)

TABLE 1. HALOCARBONS RANKED BY ESTIMATED DECREASING CHEMICAL CONTRIBUTION TO EXTINGUISHMENT.

Agent	Formula	Heat capacity		Concentration, %		Ratio calc/obs
		J/kg-K	cal/mol-K	Calculated	Observed	
HBC-30B2	CH <sub>2</sub> Br <sub>2</sub>	314.6	13.06	21.36	1.30	16.43
HBFC-21B2	CHBr <sub>2</sub> F	338.9	15.53	18.60	1.77	10.51
HBCC-30B1	CH <sub>2</sub> BrCl	406.8	12.57	22.01	2.70	8.15
BFC-12B2	CB <sub>2</sub> F <sub>2</sub>	370.8	18.58	16.03	2.17	7.39
HBFC-123aB2	CHBrFCBrF <sub>2</sub>	438.3	25.32	12.29	2.01	6.11
BFC-13B1	CBrF <sub>3</sub>	469	16.68	17.54	2.90	6.05
FIC-13I1	CF <sub>3</sub> I	361.8	16.93	17.32	3.02	5.74
FIC-115I1	CF <sub>3</sub> CF <sub>2</sub> I	448.5	26.34	11.87	2.09	5.68
BCFC-12B1	CBrClF <sub>2</sub>	452	17.85	16.58	3.22	5.15
HBFC-22B1	CHBrF <sub>2</sub>	455	14.23	19.96	4.41	4.53
HCC-280fa	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	1081	20.28	14.89	3.32	4.48
HCC-280da	CH <sub>3</sub> CHClCH <sub>3</sub>	1134.4	21.28	14.29	3.20	4.46
HBCFC-123aB1α	CBrF <sub>2</sub> CHClF	521.8	24.60	12.60	3.17	3.98
HBCFC-123B1	CF <sub>3</sub> CHBrCl	532	25.08	12.39	3.12	3.97
CFC-13	CClF <sub>3</sub>	661.5	16.50	17.69	7.22	2.45
FIC-217caI1	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	665.7	47.05	7.01	3.04	2.31
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	607	17.53	16.83	7.64	2.20
CFC-11	CCl <sub>3</sub> F	594	19.49	15.40	7.75	1.99
CC-10	CCl <sub>4</sub>	542.2	19.92	15.12	7.61	1.99
CFC-115	CClF <sub>2</sub> CF <sub>3</sub>	686.2	25.32	12.29	6.28	1.96
HCFC-124	CHClFCF <sub>3</sub>	741	24.15	12.81	6.70	1.91
HCC-150a	CH <sub>3</sub> CHCl <sub>2</sub>	769.1	18.18	16.33	8.60	1.90
HCFC-133a	CH <sub>2</sub> ClCF <sub>3</sub>	750.7	21.24	14.31	7.59	1.89
HFC-236fa	CF <sub>3</sub> CH <sub>2</sub> CF <sub>3</sub>	840.3	30.51	10.41	5.60	1.86
CFC-113	CCl <sub>2</sub> FCClF <sub>2</sub>	630	28.20	11.18	6.19	1.81
CFC-114a	CCl <sub>2</sub> FCF <sub>3</sub>	667.6	27.25	11.52	6.41	1.80
HCFC-22	CHClF <sub>2</sub>	657	13.57	20.73	11.60	1.79

TABLE 1. HALOCARBONS RANKED BY ESTIMATED DECREASING CHEMICAL CONTRIBUTION TO EXTINGUISHMENT (CONCLUDED).

Agent	Formula	Heat capacity		Concentration, %		Ratio
		J/kg-K	cal/mol-K	Calculated	Observed	
HFC-23	CHF <sub>3</sub>	737	12.32	22.35	12.60	1.77
CFC-113a	CCl <sub>3</sub> CF <sub>3</sub>	643.1	28.81	10.96	6.19	1.77
HCC-20	CHCl <sub>3</sub>	549.5	15.67	18.46	10.50	1.76
CFC-114	CClF <sub>2</sub> CClF <sub>2</sub>	710.8	29.02	10.89	6.41	1.70
HCFC-123	CHCl <sub>2</sub> CF <sub>3</sub>	711.6	25.99	12.01	7.10	1.69
HCFC-132b	CH <sub>2</sub> ClCClF <sub>2</sub>	725.6	23.39	13.17	7.85	1.68
HCC-30	CH <sub>2</sub> Cl <sub>2</sub>	598.6	12.14	22.61	14.10	1.60
FC-116	CF <sub>3</sub> CF <sub>3</sub>	760.8	25.08	12.39	7.80	1.59
HCC-130a	CCl <sub>3</sub> CH <sub>2</sub> Cl	611.3	24.51	12.64	7.96	1.59
HFC-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	808	32.81	9.76	6.30	1.55
HCFC-121	CCl <sub>2</sub> FCHCl <sub>2</sub>	602.7	26.75	11.71	7.77	1.51
FC-218	CF <sub>3</sub> CF <sub>2</sub> CF <sub>3</sub>	795	35.70	9.04	6.11	1.48
HFC-125	CHF <sub>2</sub> CF <sub>3</sub>	800	22.93	13.40	9.41	1.42
FC-14	CF <sub>4</sub>	706.7	14.86	19.28	13.79	1.40
HFC-134a	CH <sub>2</sub> FCF <sub>3</sub>	854	20.81	14.56	10.47	1.39
FC-3-1-10	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	804	45.71	7.20	5.49	1.31
HCFC-141b	CH <sub>3</sub> CCl <sub>2</sub> F	711.8	19.88	15.14	12.50	1.21
FC-C318	-CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> -	794.9	37.98	8.54	7.19	1.19

stabilized on flat burners by the cooling effect of the burner. The amount of heat removed is measured as a function of the amount of extinguishant added for a series of extinguishing agents known to operate by physical mechanisms and for a series of agents believed to operate primarily by chemical mechanisms. The characteristic curves are distinctly different for the two classes of agents, and permit the ranking of agents in order of effectiveness. For physical extinguishment, the amount of energy absorbed by an agent (and, therefore, unavailable for extraction by the burner) depends only on the agent heat capacity, giving an inverse linear relationship between the

heat extracted by the burner and the amount of agent added to the flame. For “non-catalytic” chemical extinguishment, where each agent molecule is only involved once in a suppression reaction, an inverse linear relationship is also observed, though the slope of the line varies from that observed for physical agents. Finally, “catalytic” chemical extinguishment, where each agent molecule contributes directly or indirectly (e.g., through reaction products such as HBr) in many cycles, a non-linear heat extraction curve is obtained. The technique works well both with atmospheric flames and with flames at reduced pressures (0.05 atmosphere, 5.07 kPa).

Of particular interest in this work is the observation that HFC-125 ( $\text{CHF}_2\text{CF}_3$ ) appears to act as a fuel in lean flames. A break is observed in the flammability curve when the “excess” oxygen content (above that required for reaction with the methane fuel in the flame) is equal to the HFC-125 concentration. It is proposed that Reaction 4 occurs.



The corresponding reaction for  $\text{CF}_3\text{CF}_3$  is



It, therefore, becomes of interest to examine  $\text{CF}_3\text{CF}_3$  to see whether a similar break occurs in the curve at a smaller value of “excess” oxygen. The interesting question may be this: Does the presence of hydrogen in the molecule provide a “key” for its apparent combustion? In other words, does  $\text{CHF}_2\text{CF}_3$  burn, while  $\text{CF}_3\text{CF}_3$  does not? This might not be interesting except for the fact that the heat of combustion of  $\text{CF}_3\text{CF}_3$  is almost exactly the same as that of  $\text{CHF}_2\text{CF}_3$  (based on available information and estimated heats of formation). Preliminary experiments with  $\text{CHF}_3$  shows behavior similar to that observed for  $\text{CHF}_2\text{CF}_3$  (i.e.,  $\text{CHF}_3$  acts as a fuel in the fuel-lean region); however, the break in the flammability curve does not occur at the exact point expected from Reaction 6.



### C. SYNERGISM

Mixtures of two agents, A and B, with different extinguishing capabilities, might be expected to exhibit extinguishment performance (e.g., extinguishment concentration) that changes linearly with composition. For example, a 25/75 blend of A and B might be expected to exhibit an extinguishment concentration of  $0.25[A] + 0.75[B]$ , where the square brackets denote concentration. An extinguishment concentration of a blend that is lower (better extinguishment capability) than predicted from a linear dependence is an example of synergism (Figure 3). The reverse is an example of antagonism.

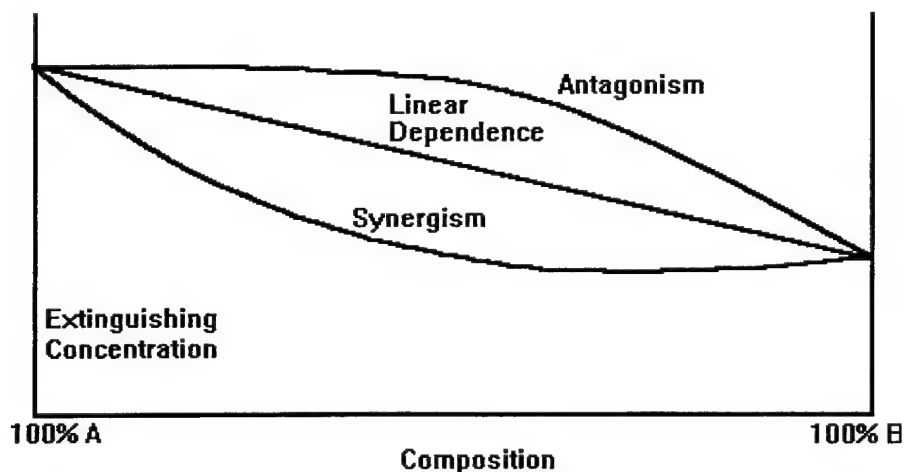


Figure 3. Synergism.

Synergism is often observed in fire extinguishment. Mixtures of haloalkanes with propellants have been shown to exhibit synergism (Reference 19). In fact, one study of a number of halocarbon blends found only synergism, with no observations of a linear dependence or of antagonism (Reference 20).

### D. DRY CHEMICAL FIRE SUPPRESSION

Certain finely ground powders can be used as extinguishing agents. The extinguishing mechanism is complex and not fully understood (*vide infra*). Sodium bicarbonate was one of the first dry chemical extinguishants to be used. Potassium bicarbonate ( $\text{NaHCO}_3$ ) and mono-

ammonium phosphate  $[(\text{NH}_4)\text{H}_2\text{PO}_4]$  were developed later in the 1960s. These powders typically have particle sizes of less than  $10\text{ }\mu\text{m}$  up to  $75\text{ }\mu\text{m}$  with average particle sizes of 20 to  $25\text{ }\mu\text{m}$ .

Dry chemicals generally provide very rapid knockdown of flames and are more effective than halons in most applications (Reference 21). The main disadvantages of dry chemical fire extinguishants include (1) poor penetration behind obstacles, (2) no inhibiting atmosphere after discharge, (3) no direct cooling of surfaces or fuel,\* (4) secondary damage to electronic, electromechanical, and mechanical equipment, (5) cleanup problems, and (6) temporary loss of visibility if discharged in a confined space.

Fixed dry chemical systems are very uncommon; uses are normally limited to "localized applications," such as with textile machines or deep fat fryers, for which halons would not normally be used. Dry chemical extinguishers are suitable for Class A, B, and, in some cases, C fires depending on the type of powder used. Powder extinguishers are often suitable substitutes for halon with fires of flammable liquids. They are also suitable for situations where a range of different fires can be experienced (e.g., electrical fires, flammable liquid fires, and fires in solids). In this respect, powder extinguishers resemble halon extinguishers. Three mechanisms have been proposed to explain extinguishment by particulates:

The homogeneous mechanism proposed is that certain particulates vaporize to give molecular species that act as chemical fire suppressants. These species may act like halogen-containing molecules to remove flame free radicals (e.g., Section VI).

There is considerable evidence that many dry chemical agents operate primarily by heat absorption (Reference 9). This may occur by thermal decomposition and particle heating. In some cases, particles may also remove heat by thermal radiation following absorption of heat.

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\*Cooling of the flame due to thermal decomposition has been proposed as a mechanism for flame suppression by dry chemical agents; however, this is somewhat different from the direct cooling of surfaces, fuel, and flames by an agent such as water where cooling occurs in the absence of flame/agent interaction.



Finally, free radical recombination may occur on particle surfaces. A number of studies have indicated temperature increases on particulate surfaces that is compatible with free radical recombination (References 22-26).

#### E. PARAMAGNETIC INHIBITORS

A mechanism that has not been previously proposed is that paramagnetic species, such as iron atoms, could catalyze some normally spin-forbidden reaction or, at least, equilibrate spin states. One paramagnetic species that is involved in combustion is the oxygen ground-state triplet ( $^3\text{P}$ ), which is separated from the excited state singlet ( $^1\text{D}$ ) by about 190.1 kJ/mol (45.4 kcal/mol). These may not be in equilibrium in a fire.  $\text{O}(^1\text{D})$  is much more reactive with various species than is  $\text{O}(^3\text{P})$ . For a series of reactions of the type shown in Reaction 7, the rate constants increase by  $10^{+3}$  to  $10^{+8}$  on going from triplet to singlet oxygen (Table 2, Reference 147).



A paramagnetic species such as an iron atom might (1) effect relaxation of more reactive  $\text{O}(^1\text{D})$  to less reactive  $\text{O}(^3\text{P})$  assuming that there is a nonequilibrium mixture of the two states formed in a fire or (2) allow normally forbidden reactions of  $\text{O}(^3\text{P})$  with inhibitor species.

An alternative mechanism could be one in which brief bonding with a paramagnetic particle or third-body molecule would catalyze the normally spin-forbidden conversion of a triplet to a singlet state in an activated complex. For example, the reaction of hydrogen atoms on a particulate surface could be aided if the particle were paramagnetic (Reaction 8).

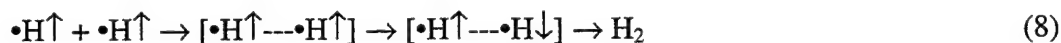


TABLE 2. RATE CONSTANTS FOR REACTIONS OF  
SINGLET AND TRIPLET OXYGEN ATOMS.

Reactant	Rate constant, $k_{298K}$ , cc molec-1 s-1	
	O( <sup>1</sup> D)	O( <sup>3</sup> P)
H <sub>2</sub>	$1.1 \times 10^{-2}$	$3.5 \times 10^{-18}$
CH <sub>4</sub>	$1.4 \times 10^{-10}$	$2.7 \times 10^{-18}$
CHCl <sub>3</sub>	$3.0 \times 10^{-10}$	$8.3 \times 10^{-16}$
CHF <sub>3</sub>	$1.9 \times 10^{-12}$	$<3.7 \times 10^{-15}$
HCl	$1.5 \times 10^{-12}$	$1.4 \times 10^{-16}$
HBr	$1.48 \times 10^{-10}$	$3.7 \times 10^{-14}$
NH <sub>3</sub>	$2.5 \times 10^{-10}$	$1.1 \times 10^{-16}$
H <sub>2</sub> S	$2.5 \times 10^{-10}$	$1.8 \times 10^{-14}$

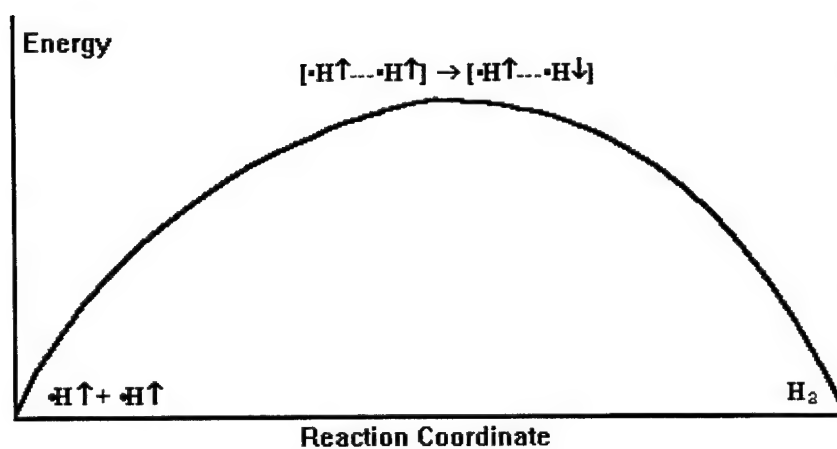


Figure 4. Activation Energy for Hydrogen Atom Recombination.

## F. ION MECHANISMS

Reactions of positive ions known to be present in hydrocarbon flames have been studied at 300 K and 525 K (Reference 27). Rate constants and product branching percentages have been determined for reaction of Halon 1301 with  $\text{HCO}^+$ ,  $\text{CH}_3^+$ , and  $\text{CH}_5^+$ . These reactions give  $\text{CF}_3^+$  and  $\text{CF}_2\text{Br}^+$ . The ions  $\text{H}_2\text{COH}^+$ ,  $\text{H}_3\text{COH}_2^+$ , and  $\text{H}_3\text{O}^+$  were unreactive with Halon 1301. In addition, reactions of  $\text{CF}_3^+$  and  $\text{CF}_2\text{Br}^+$  with selected hydrocarbons were studied. It was concluded that no evidence was found to indicate that ions play a role in flame inhibition by Halon 1301. The one suppression area where ions may be involved is the reported effect of electric fields on flames (References 28-32).

## G. EXPLOSION PREVENTION (INERTION)

Like a fire, an explosion, generally cannot occur without the four legs of the fire tetrahedron—fuel, oxygen, heat, and sufficient free radicals to sustain the reaction. Unless sufficient fuel is available (at the Lower Flammability Limit or LFL) or sufficient oxygen is available (at the Upper Flammability Limit or UFL), the mixture is nonflammable. Unless the temperature reaches the ignition temperature, and heat is conveyed to the next layer of unburned gas, the mixture is also nonflammable. Finally, unless an adequate concentration of free radicals is available to sustain the reaction, the mixture is also nonflammable. Thus, most of the discussion presented earlier in this section on fire suppression is believed to hold for explosion inertion as well.

An explosion sphere is often employed in testing agents for ability to inert fuel/air mixtures. Table 3 shows results for testing of the inerting ability of several physically active and chemically active agents using propane as a fuel (Reference 33). Inertion is defined as having occurred when the explosion overpressure is 1 psi or below.

It is obvious by the above table that the stoichiometric inertion concentration can vary by a significant amount for physical action agents, reflecting the fact that no agent is a 100 percent chemical action agent or a 100 percent physical action agent.

TABLE 3. TYPICAL PROPANE INERTION RESULTS  
FROM EXPLOSION SPHERE TESTING.

Chemical	Stoichiometric Inertion Concentration, % by volume
Physical Action Agents	
Nitrogen	38.0
Carbon Dioxide	29.7
HFC-23	19.5
HFC-227ea	12.7
FC-6-1-16	6.5
Chemical Action Agents	
Halon 1301	4.3
FIC 13I1	5.2

The U.S. Army has conducted inerting experiments with eight Halon 1301 replacement candidates using butane/air mixtures (Reference 34). The results are shown in Table 4. Here inertion is defined as giving zero overpressure in an explosion sphere.

#### H. EXPLOSION SUPPRESSION

Unlike explosion prevention, explosion suppression refers to extinguishment of an explosion once it has been initiated. Since this process occurs within several tenths of a second, rapid sensing of the impending explosion and release of the suppressing agent is critical in extinguishing the flame front and preventing the explosion from causing damage. Halon 1301 is used in aircraft dry bays and fuel tanks to prevent an explosion caused by hostile action or accident from destroying the aircraft. Halon is also used in areas with flammable dusts such as grain elevators.

TABLE 4. AGENT CONCENTRATIONS REQUIRED TO INERT A BUTANE/AIR MIXTURE.

Agent	Formula	Concentration, % by volume
Perfluoroethyl Iodide	$\text{CF}_3\text{CF}_2\text{I}$	4.38
Halon 1301	$\text{CF}_3\text{Br}$	4.49
Perfluoroheptane	$\text{C}_7\text{F}_{16}$	4.66
Perfluoro-2-butyltetrahydrofuran	$\text{C}_4\text{F}_{11}(\text{C}_4\text{F}_7\text{O})$	4.70
Perfluorohexane	$\text{C}_6\text{F}_{14}$	4.75
Perfluoromethylcyclohexane	$\text{CF}_3\text{C}_6\text{F}_{11}$	5.60
2,2-Dichloro-1,1,1-trifluoroethane (HCFC-123)	$\text{CHCl}_2\text{CF}_3$	6.78
Perfluorobutane	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$	7.90
2-Bromo-1,1-difluoroethene	$\text{CF}_2=\text{CHBr}$	9.32

The mechanisms of explosion suppression are not as well defined as those for fire suppression. There is good evidence, however, that explosion suppression by chemical agents may be primarily due to heat absorption rather than to any chemical mechanism. For example, in aircraft dry bay explosion suppression, perfluoropropane ( $\text{C}_3\text{F}_8$ ) is better than Halon 1301 and perfluoromethane ( $\text{CF}_4$ ) is about equivalent.\* This is what would be predicted from the vapor-phase heat capacities. The heat capacities of perfluoromethane and Halon 1301 are similar [62.2 J/mol-K (14.9 cal/mol-°C, Reference 35) and 69.84 J/mol-K (16.68 cal/mol-°C, Reference 36), respectively, both at 25 °C and 760 Torr pressure]. The heat capacity of perfluoropropane is significantly higher [149.5 J/mol-K (35.7 cal/mol-°C, Reference 36)].†

Testing must be accomplished at large scale due to the effect of the test vessel size on the sensing of the explosion and release of the agent in sufficient time to allow extinguishment prior

\*Fett, C. E., U. S. Air Force Wright Laboratories, Wright-Patterson AFB, Florida, personal communication to Robert E. Tapscott, NMERI, 17 April 1992.

†CEA-308, personal communication to Robert Tapscott from John Pignato, 3M Company, St. Paul, Minnesota, 17 November 1994.

to the flame front reaching the vessel wall. Testing at these scales is expensive due to the size of the apparatus and amount of agent required to conduct tests.

## I. FLAME RETARDANTS

Flame retardants are chemicals that impregnate materials such as cellulosic fabrics or are incorporated into polymers to provide flame resistance. Though such materials are not used to extinguish fires or explosions, their extinguishment mechanisms may provide some insights into possible halon substitutes. Some definitions follow:

1. Flameproofing agent: A chemical that is applied to a material to make it resistant to fire initiation. This is often taken as synonymous to a flame retardant. The flameproofing agent might be applied to the material as a sprayed-on coating or embedded into the material as it is fabricated. Examples of flameproofing agents are polybrominated biphenyl (PBB) and antimony oxide.

2. Fire retardant: A chemical that is applied to a material that will retard the development of fire on that material. As with a flameproofing agent, the fire retardant might be applied to the material as a sprayed on coating or embedded into the material as it is fabricated.

3. Flame-resistant material: A material that is resistant to the development of a fire. In this case, the material itself might be the desired object of fire-resistance such as fire-resistant rubber or hydraulic fluid. Alternatively, the flame-resistant material might be applied to another material to confer the desired overall property of flame resistance or it might be embedded into a material as it is fabricated.

Five of the most common types of flame retardants are alumina trihydrate, antimony oxide, bromine compounds, chlorine compounds, and phosphorus compounds (Reference 37). The function of these retardants is quite different from that of halons and other fire extinguishants. Flame retardants are always incorporated into a material to hinder initiation of a fire or to limit burning. Extinguishants, on the other hand, are applied after a fire or explosion has been initiated, or to give explosion protection in an area. Of particular importance is that

most fire extinguishants and suppressants give, at least some, multidimensional fire and explosion protection.

## SECTION IV

### AGENT APPLICATION METHODOLOGIES

#### A. AEROSOLS

Aerosols are receiving increased attention (Reference 38). Two types of aerosols are of particular interest: water mists (Reference 39) and particulate aerosols, in particular pyrotechnically generated aerosols (see, e.g., Reference 40 and footnote).<sup>\*</sup> Fine halocarbon mists have also been shown to provide highly effective fire extinguishment (References 41 and 42).

#### B. ENCAPSULATION

Encapsulation has been used to apply fire suppressants; however, it must be noted that such methods do not allow the use of agents that have been restricted due to ozone depletion.

Brominated alkanes such as 2,2,3,3-tetrabromobutane have been microencapsulated in formaldehyde-melamine resins for use in fireproofing (Reference 43), and microencapsulated organohalogen agents have been evaluated in a propane/air diffusion flame (Reference 44).

One possible way of encapsulating an extinguishant is by intercalation with graphite. Graphite, which consists of 2-dimensional sheets of interconnected hexagonal C<sub>6</sub> rings, is capable of absorbing compounds between the sheets, which are held together by relatively weak bonds. The products are known as intercalation compounds. Intercalation compounds of graphite have been used in extinguishment of metal fires (Reference 45). In this case, however, the compounds were used only to allow production of exfoliated (expanded ) graphite, which actually provided the extinguishment.

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<sup>\*</sup>Sheinson, R. S., Eaton, H. G., Zalosh, R. G., Black, B. H., Brown, R., Burchell, H., Salmon, G., and Smith, W. D., "Fire Extinguishment by Fine Aerosol Generation," 1993 International Conference on CFC and Halon Alternatives Washington D.C., October 20-22, 1993. (Unpublished)



### C. CLATHRATES

Agents can also be encapsulated by clathrate formation. Clathrates are compounds that exhibit encapsulation at the molecular level. This could improve both deliverability and, in some cases, performance. One excellent example is the formation of gas hydrates in which a gaseous molecule is enclosed in a cage of water molecules. Gas hydrates have been reported for dibromodifluoromethane, Halon 1211, and Halon 1301, all of which form hydrates with the approximate formulas  $CX_4 \cdot 17H_2O$ . These materials have been proposed as fire suppression agents with a decreased vapor pressure (improved deliverability) and an increased heat absorption capacity due to an increased heat of vaporization (improved fire suppression possible) (Reference 46). The heats of vaporization ( $\Delta H_{vap}$ ) of the pure halocarbons and of the hydrates are compared in Reference 46. The formation of these hydrates, however, requires low temperatures, and a method would have to be found to maintain the hydrates in a stable form prior to delivery. A number of clathrates, however, are stable at room temperature. For example, urea forms clathrates with a number of materials.

TABLE 5. HEATS OF VAPORIZATION OF SELECTED HALOCARBONS AND THEIR HYDRATES AT 0 °C.

Halocarbon	$\Delta H_{vap}$ of halocarbon, kJ/mol (kcal/mol)	$\Delta H_{vap}$ of hydrate, kJ/mol (kcal/mol)
$CBR_2F_2$	26.21 (6.26)	863.90 (206.34)
$CBrClF_2$	23.15 (5.53)	861.39 (205.74)
$CBrF_3$	14.32 (3.42)	857.21 (204.74)

### D. GELS

A number of gel compositions containing halocarbons have been reported (References 47-50). The SNAP list gives variety of formulations under the category "gelled halocarbon/dry chemical suspension" (designated as "Powdered Aerosol B" in the first SNAP listing) developed for particular markets. Each blend contains one or more halocarbons, a dry chemical, and a gel that keeps the powder and gas uniform. The materials, have been tested in a number of

applications, including tracked vehicles (References 51 and 52). Testing to date indicate that at least some formulations have an effectiveness similar to or better than that of Halon 1301 on either a weight basis or a storage volume basis.\*

#### E. AMBIENT CONDITIONS

The effects of varying pressure (760 to 132 torr) on the efficiency of bromomethane ( $\text{CH}_3\text{Br}$ ), iodomethane ( $\text{CH}_3\text{I}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) as inhibitors of laminar premixed ethylene-air mixtures have been measured. For all of the compounds except  $\text{CH}_2\text{Cl}_2$  (for which there is no change), the inhibition effectiveness decreased by approximately 40 percent with a decrease in pressure to 132 torr.

#### F. LOCATION OF INTRODUCTION

A number of studies have determined a difference in agent effectiveness depending on the location of introduction of an agent. Significant differences have been observed when  $\text{CHBr}_3$  is introduced into the air or fuel side of a propane/air diffusion flame of an opposed-jet burner, with a better efficiency in the air side (Reference 44).

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\*Moore, T. A., "An Evaluation of Envirogel™ as a Halon Alternative," International CFC and Halon Alternatives Conference, Washington, DC, USA, 23-25 October 1995. (Unpublished)

## SECTION V

### CHEMICALS AND CHEMICAL FAMILIES

A number of reports and publications have been prepared reviewing fire suppressants. An early, but informative report presents information on fire suppressant patents (Reference 53). There have also been numerous analyses of potential halon replacements (e.g., Reference 54), but none of these consider all compounds containing all elements. Therefore, selection and analysis of suitable agents has been conducted by periodic table family (Figure 5). Each group is described and an analysis is made of its potential to include suitable fire fighting agents. Groups I and II have been combined because of their similarity.

I    II		III   IV   V   VI   VII   VIII											
		<div>H</div>					<div>He</div>						
Li	Be	<div>Transition Metals</div>						B	C	N	O	F	Ne
Na	Mg							Al	Si	P	S	Cl	A
K	Ca							Ga	Ge	As	Se	Br	Kr
Rb	Sr							In	Sn	Sb	Te	I	Xe
Cs	Ba							Tl	Pb	Bi	Po	At	Rn
Fr	Ra												

## SECTION VI

### COMPOUNDS OF GROUP I AND GROUP II ELEMENTS

Group I elements comprise the alkali metals—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Group II elements are the alkaline earths—beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). A detailed review of fire extinguishment by compounds of the Group I and II elements is contained in a general report on metal compounds as candidates for streaming agents (Reference 55).

#### A. ALKALI METALS

##### 1. Chemistry and Fire Suppression

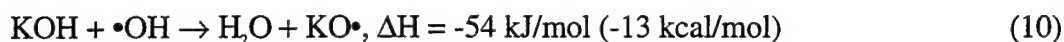
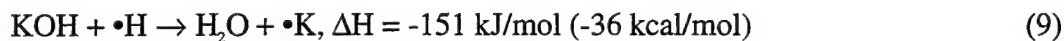
With a few exceptions (primarily, intermetallic compounds and alloys), alkali metal compounds are ionic solids. Their present use in fire extinguishment is, therefore, limited to dry chemical extinguishants. The chemistry of the alkali metal compounds is primarily the chemistry of the alkali metal cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Fr}^+$ ) with the chemistry of the accompanying anion. The alkali metal cations coordinate best with oxygen donating ligands. For this reason, many if not most alkali metal compounds are hydrated with water in the cation coordination sphere.

The flame suppression effectiveness of alkali metal salts follows the order  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$  (Reference 56). Sodium and potassium salts have been widely used in dry chemical extinguishants. Many dry chemicals have a greater weight effectiveness than the halons in current use, at least for some applications (Reference 21). Sodium bicarbonate ( $\text{NaHCO}_3$ ), like monoammonium phosphate  $[(\text{NH}_4)\text{H}_2\text{PO}_4]$ , is an excellent explosion suppressant. It is also used in stove-top fire extinguishers and is the largest selling dry chemical, primarily because of its low cost and its use in training. Potassium bicarbonate ( $\text{KHCO}_3$ ) is also a widely used dry chemical fire extinguishant. It is widely recognized that the amount of carbon dioxide released by the carbonate agents in fires is insufficient to explain the fire suppression ability, which must be attributed to other mechanisms (Reference 57). Potassium carbonate ( $\text{K}_2\text{CO}_3$ ), potassium

bicarbonate, and Monnex (urea potassium carbonate) are all better than Halon 1211 or Halon 1301 for delaying hot-surface reignition, and potassium dawsonite  $[\text{NaAl}(\text{OH})_2\text{CO}_3]$ , potassium chloride (KCl), and potassium iodide (KI) may be even more effective (Reference 58). Iodide salts have been shown to be very effective at low temperatures, with the effectiveness dropping off at higher temperatures (Reference 59).

In general, potassium salts are more effective than sodium salts in fire suppression (Reference 60). In part, this may be due to the lower lattice energies for potassium salts compared with sodium salts; however, this does not explain all of the difference observed. Moreover, effectiveness for preventing reignition of jet fuel on a 775 °C (1427 °F) hot surface gives the rank order  $\text{K}_2\text{CO}_3 > \text{KHCO}_3 > \text{KCl} > \text{NaHCO}_3 > \text{Na}_2\text{CO}_3 > \text{NaCl}$  (Reference 61). Note, however, that this may be primarily due to differences in glass forming and coating ability, rather than to chemical extinguishment effectiveness.

It has been proposed that alkali metal salts decompose to give simple species that scavenge free radicals. Some possible reactions for potassium are shown in Reactions 9 through 12 (Reference 60). Reactions involving the union of two species, such as Reactions 11 and 12, are less likely since a three-body reaction is required.



Salts such as potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4$ ) and potassium hexacyanoferrate(II) [potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ ] are significantly better flame suppressants than the carbonates, apparently due to their ease of decomposition in a flame to give small particles and/or free-radical capturing species.

The addition of only 0.1 percent by weight of lithium nitride ( $\text{Li}_3\text{N}$ ) to a propellant suppresses afterburning in a rocket exhaust (Reference 62). This can be compared to the requirement of a few percent of bromine ( $\text{Br}_2$ ) to give the same effect.

Alkali metals have also been introduced into flames as solutions. Sprays of aqueous solutions containing 60 percent potassium lactate or 60 percent potassium acetate are far superior to neat water sprays in extinguishing JP-8 fuel fires (Reference 63).<sup>\*</sup> The improved performance is attributed to the release of solid salts upon evaporation of the water droplets. Lithium 2,4-pentanedionate(-1) [lithium acetylacetonate,  $\text{Li}(\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3)$ ] is very effective on a mass basis in extinguishing ethanol flames when introduced as an aerosol of an ethanol solution (Reference 56).

## 2. Environmental Characteristics

Environmental concerns about the alkali metal cations themselves are minimal. They have little terrestrial environmental impact except at high concentrations (in many cases, very high), and have no known global environmental effects. Any environmental problems will be due almost entirely to the (normally) anionic components. Thus, for example, the environmental impact of sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) is due to the chromium in the chromate anion.

## 3. Toxicity

With the exception of lithium and francium (radioactive), toxicities of the alkali metal cations are very low to moderate. Sodium and potassium cations are normally physiological constituents. Lithium compounds are used for treating mania and depression. Lithium cation is a central nervous system (CNS) toxicant, causing dizziness, prostration, anorexia, apathy, and nausea (Reference 64). At higher concentrations,  $\text{Li}^+$  can cause death. The oral lethal dose of lithium chloride ( $\text{LiCl}$ ) in humans is approximately 200 mg/kg (Reference 65). Rubidium and cesium cations substitute for potassium as intracellular ions and are moderately toxic by ingestion. Both are somewhat less toxic than lithium. In most cases, any toxicity of alkali metal compounds can be attributed to the accompanying anion.

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<sup>\*</sup>JP-8 is a hydrocarbon fuel with a flash point typically about 50 °C. The fuel in the study cited here had a flash point of 50 °C.

## B. ALKALINE EARTHS

### 1. Chemistry and Fire Suppression

With the exception of beryllium compounds and like the alkali metal compounds, compounds of the alkaline earths are, for the most part, ionic solids. Thus the chemistry of alkaline earth compounds is primarily the chemistry of the alkaline earth cations ( $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Ra}^{+2}$ ) with the chemistry of the accompanying anion. Note, however, that bonding in many magnesium compounds probably has some significant covalent character. There is no definitive proof that any of the alkali metals exist in a +1 oxidation state.

Beryllium compounds are definitely highly covalent. In fact, there is little evidence for a discrete  $\text{Be}^{+2}$  cation. A number of ionic compounds containing  $\text{Be}(\text{H}_2\text{O})_4^{+2}$  are known. The chemistry of beryllium is very complex, and beryllium forms more compounds than any other alkaline metal. However, owing to the toxicity of this element, there is little reason to review this chemistry here.

There is little evidence that compounds of the alkaline earths could provide effective fire extinguishants, at least due to the presence of the alkaline earth itself. Calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ], calcium carbonate ( $\text{CaCO}_3$ ), calcium fluoride ( $\text{CaF}_2$ ), and talc [ $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ] are ineffective extinguishants of premixed methane/air flames compared with potassium and sodium salts (Reference 66). Calcium carbonate is ranked below the common dry chemical extinguishants and even below sodium chloride ( $\text{NaCl}$ ) (Reference 67). On the other hand, alkaline earth salts cause significant catalysis of free radical recombination rates in fuel-rich, premixed  $\text{H}_2/\text{O}_2/\text{N}_2$  flames with effectiveness increasing in the order  $\text{Mg} = \text{Ca} < \text{Sr} < \text{Ba}$  (Reference 68).

## 2. Environmental Characteristics

Like the alkali metal cations, environmental concerns about the alkaline earth cations are minimal. Beryllium, barium and radium (radioactive) compounds are on the Community Right to Know List. The remaining alkali metal compounds have little terrestrial environmental impact except at high concentrations (in many cases, very high), and have no known global environmental effects. Any environmental problems will probably be due to the anion.

## 3. Toxicity

With the exception of radium, beryllium and, to a lesser extent, barium, the toxicity of the alkaline earth cations is for the most part low. Beryllium and its compounds are human and experimental carcinogens, tumorigens, and neoplastigens. The compounds can enter the body through inhalation of dusts and cause skin ulceration. Breathing the compounds can cause chronic lung disease. Magnesium and calcium are both required for normal physiologic functioning and are believed to cause no systemic poisoning. Strontium compounds are moderately toxic by ingestion. Soluble barium compounds are poisonous.

## C. CONCLUSIONS AND RECOMMENDATIONS

Due to cost, toxicity, or both, only compounds of the elements sodium, potassium, magnesium, calcium, and, possibly, lithium can be considered as fire extinguishants. On the other hand, there appears to be little to recommend the alkaline earths or lithium. The high efficiency of potassium compounds make them very attractive as extinguishants; however, since potassium compounds that are gaseous or highly volatile at room temperature are unknown, such materials are unlikely replacements for total-flooding Halon 1301 systems across the broad range of applications. This is particularly true for explosion inertion. Potassium and sodium dry chemical extinguishants are, of course, attractive as replacements for Halon 1211 in many streaming applications. They are already employed extensively in such uses and their use is liable to increase.



Two recent advances in technology have made potassium salts capable of filling some total-flood applications. First, pyrotechnically generated aerosols permit the production of very fine particulates of potassium compounds (References 69-72). The aerosol products have some, but by no means all, of the attributes of a total-flood agent. Second, there has been some research on the production of extremely fine particulates using a freeze drying column. Nevertheless, alkali metal and alkaline earth compounds offer little promise as a replacement for Halon 1301 without significant, perhaps massive, retrofit.

## SECTION VII

### COMPOUNDS OF GROUP III ELEMENTS

The elements boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl) comprise the Group III family of elements. The +3 oxidation state is by far the most common for these elements with the exception of thallium, where the most common oxidation state is +1. Little evidence exists for the presence of a simple +3 ion in compounds of any of these elements.

#### A. BORON COMPOUNDS

##### 1. Chemistry and Fire Suppression

Boron compounds are highly covalent. A common geometry is exhibited by three-coordinate trigonal planar compounds such as boron trifluoride ( $\text{BF}_3$ ). Although the formula for this compound can be written with only single  $\text{sp}^3 \leftrightarrow \text{sp}^2$   $\sigma$  bonds (Figure 6) between the boron and the fluorine (structure I in Figure 7), the presence of an unfilled p orbital on boron and lone pairs on fluorine make fluorine to boron  $\text{p}\pi \rightarrow \text{p}\pi$  back bonding possible (Figure 6).<sup>\*</sup> This is shown for one tautomeric form only in Structure II in Figure 7, where the formal charges are shown.

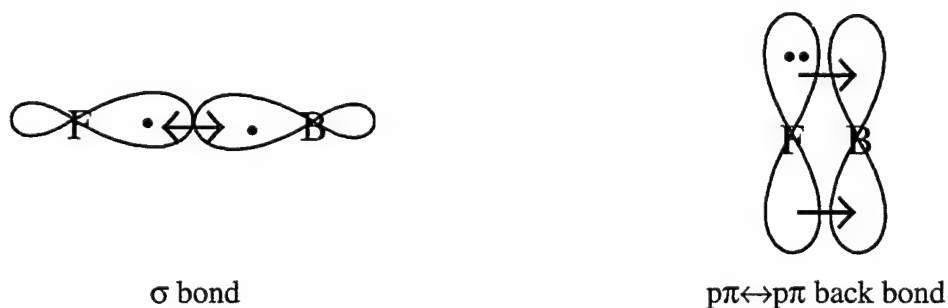


Figure 6. Bond Types in Boron Trifluoride.

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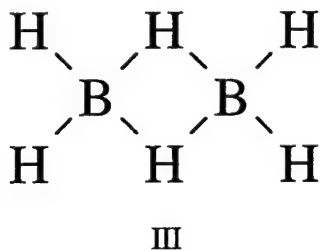
<sup>\*</sup>Actually since the filled orbitals on fluorine are probably  $\text{sp}^3$ , this might be termed " $\text{sp}^3 \pi \rightarrow \text{p}\pi$ " bonding; however, it is most commonly termed simply " $\text{p}\pi \rightarrow \text{p}\pi$ " since the actual degree of hybridization is uncertain. For simplicity, much of the bonding discussed in this report is presented using a valence bond (VB) description. It is recognized, however, that this may be overly simplistic.



Figure 7. Boron Trifluoride.

The tendency for boron to complete an octet is very strong. Boron easily bonds with four fluorine atoms to form the very stable tetrahedral tetrafluoroborate anion ( $\text{BF}_4^-$ ). In an extensive study of boron compounds, sodium tetrafluoroborate ( $\text{NaBF}_4$ ) was the most effective single compound for reducing fabric flammability (Reference 73).

In the case of the hydrides where there are no lone pairs on hydrogen, back bonding to satisfy the desire of a boron to complete an octet is impossible. Thus, the simplest hydride is not  $\text{BH}_3$ , but is  $\text{B}_2\text{H}_6$  (III, diborane), where the boron attempts to increase its valency by dimerization. Note that the structure of diborane cannot be described in simple two-atom valence bond (VB) terms as done for  $\text{BF}_3$ , however. A polyatomic molecular orbital (MO) description is needed.



The chemistry of the boron hydrides is exceedingly complex. Simple boranes are highly reactive. These materials thermally decompose, react with water, and ignite readily. Boron hydride derivatives, such as the carboranes, are more stable; however, there is little reason to believe that any borohydrides will act as fire suppressants without the presence of some fire

suppressing group such as iodine, bromine, or a metal atom. The borohydrides are electron deficient as are free radicals, and no unique interaction is expected.

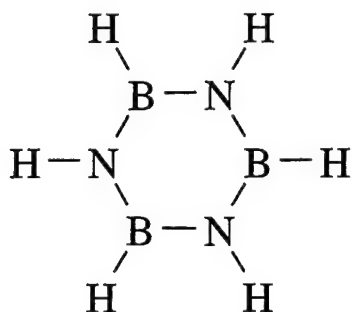
Boron exhibits a complex chemistry of solid borate compounds containing boron-oxygen bonds. Borates and related compounds have been used as flame retardants for cellulosic products and for polymers. The chemistry of borates is complicated. They are oligomers of the  $\text{BO}_3^{-3}$  ion, and exist as both chains and rings. The stoichiometric ratio of  $\text{Na}_2\text{O}$  to  $\text{B}_2\text{O}_3$  has often been used to classify borates. Thus, 1:1, 1:2, and 1:5 ratios give the metaborates, tetraborates, and pentaborates, respectively. Common flame retardants are sodium borate pentahydrate (borax pentahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ ), boric acid  $[\text{B}(\text{OH})_3]$ , boric oxide ( $\text{B}_2\text{O}_3$ ), disodium octaborate tetrahydrate ( $\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$ ), ammonium pentaborate octahydrate  $[(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}]$ , and zinc borates (e.g.,  $\text{Zn}_4\text{B}_{12}\text{O}_{22} \cdot 7\text{H}_2\text{O}$ ) (Reference 74). In particular, the zinc compounds have been used extensively in the plastics and rubber industries.

Boron oxide compounds (borates, boric oxide, and boric acid) appear to operate in two ways, both of which provide primarily physical extinguishment. First, the hydrated materials release water and melt in endothermic reactions to provide cooling.\* The ammonium compound may also undergo endothermic dissociation to provide cooling. Second, the boron compounds form glasses to provide a coating over the char formed in a flame. In particular, boric oxide (formed from several of the boron compounds) readily forms a low melting glass that inhibits oxygen permeation. It has also been proposed that borates can react with the  $\text{C}_6$ -hydroxyl group of a cellulosic material to form a borate ester that blocks the release of flammable  $\text{C}_6$  fragments.

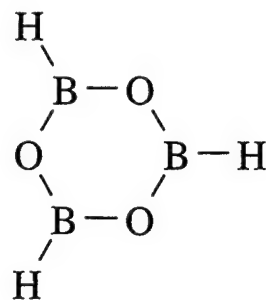
Two particularly interesting molecular systems are those based on the borazole (IV) and boroxole (V) molecules. Liquid borazole decomposes very slowly at room temperature. It is unreactive toward air and oxygen unless sparked, and slowly hydrolyzes to hydrogen, ammonia, and boric acid in the presence of water. Both borazole and boroxole exhibit some delocalized  $\pi$  bonding over the rings due to the presence of  $p\pi \rightarrow p\pi$  back bonding between the nitrogen or oxygen lone pairs and boron. Note the electronic similarity between the boroxole

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\*Anhydrous  $\text{B}_2\text{O}_3$  partially hydrates during processing and use.



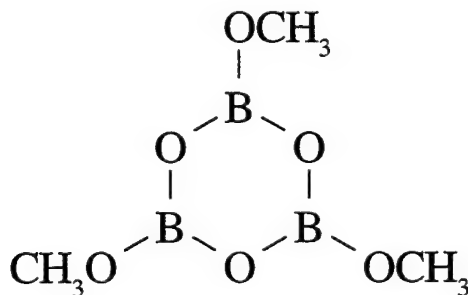
IV



V

and, in particular, the borazole molecules and the cyclic phosphorus nitrides discussed in Section IX. These compounds are all isoelectronic.

A large number of substituents can be used in place of hydrogen on the borazole and boroxole rings, and many of the derivatives are volatile liquids. Liquid trimethoxyboroxine (VI, TMB) has been shown to extinguish magnesium, titanium, zirconium, and small sodium and sodium-potassium fires (References 75 and 76). The TMB provides a coating of boric acid (and/or hydrated boron oxides) over the surface of the burning metal. Since TMB is flammable, a mixture with Halon 1211 has been developed as a metal fire extinguishant (References 77 and 78). Boroxine hydrolyzes readily to produce boric acid and methanol (Reaction 13). Other derivatives, such as trimethylboroxine  $[(CH_3)_3B_3O_3]$ , Reference 79] and trifluoroboroxine  $(F_3B_3O_3)$ , Reference 80) are known.



VI



## 2. Environmental Characteristics

Borates are a common component of many soils and they are unlikely to pose any significant terrestrial environmental impact. There is no reason to expect boron compounds to exhibit any significant global environmental impact owing to the presence of boron itself.

## 3. Toxicity

Though borates and boric acid are widely used, boron compounds are moderately toxic. The fatal oral dose of boric acid for an adult is somewhat greater than 15 to 20 g and is somewhat less for infants (Reference 81).

Trimethoxyboroxine produced slight lethargy to rats with nine 6-hour exposures at 600 ppm; however, autopsies showed normal organs (Reference 82). Methanol released by hydrolysis in the lungs (Reaction 13) is likely to make this material exhibit some toxicity.

## B. ALUMINUM COMPOUNDS

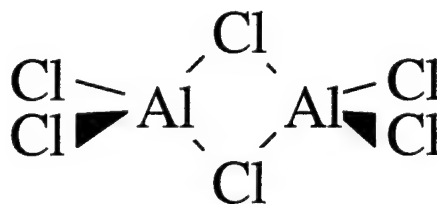
### 1. Chemistry and Fire Suppression

There is some evidence for aluminum with oxidation states of +1 and +2; however, nearly all common aluminum compounds exhibit oxidation states of +3. Aluminum compounds are significantly more ionic than are boron compounds; however, many aluminum compounds are highly covalent. The chemistry of aluminum is much less complex than that of boron, and many fewer compounds are known.

Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is highly stable and unreactive. Aluminum oxide trihydrate ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) is widely used as a fire retardant for elastomers (Reference 37), where it operates primarily by endothermic release of water to provide cooling.

Like boron compounds, aluminum compounds are often electron deficient (i.e., there are insufficient electrons present to provide an octet of electrons to aluminum in a simple VB description). Thus, aluminum chloride does not exist as a simple  $\text{AlCl}_3$  molecule. In the gas phase, the compound is dimeric (VII,  $\text{Al}_2\text{Cl}_6$ ) allowing aluminum to achieve an octet by accepting a lone pair from bridging chlorine atoms. Gaseous aluminum chloride is an effective

inhibitor of premixed methane/air flames (Reference 83), and the dispersed powder effectively inhibits spark ignition of methane/air mixtures (Reference 84). This activity may, however, be due to the presence of chlorine rather than to any inherent fire extinguishing capability of the aluminum itself.



VII

The addition of carrier matrixes containing oxy or hydroxy derivatives of aluminum, such as sodium and potassium dawsonite  $[\text{NaAl}(\text{OH})_2\text{CO}_3]$  and  $[\text{KAl}(\text{OH})_2\text{CO}_3]$  to iodide salts, appears to give synergism and enhances the agent performance (Reference 59). Note, however, that this introduces sodium or potassium cations, which may provide the enhancement.

## 2. Environmental Characteristics

Aluminum is a common constituent of soils and minerals and is unlikely to pose any significant environmental impact. Aluminum compounds are also unlikely to pose any global environmental threat due to the aluminum itself.

## 3. Toxicity

Although aluminum is probably not a systemic poison, a number of aluminum compounds are irritants or are toxic owing to the presence of other components. Aluminum chloride hexahydrate  $(\text{AlCl}_3 \cdot \text{H}_2\text{O})$  is an experimental tetratogen.

## C. OTHER GROUP III COMPOUNDS

### 1. Chemistry and Fire Suppression

Gallium, indium, and thallium are relatively rare elements. The chemistry becomes increasingly metallic as one proceeds from gallium to thallium. The tendency to exhibit

a +1 oxidation state increases in this same order, and, for thallium, the +1 oxidation state is more common than the +3 state. No fire extinguishment studies on compounds of gallium, indium, or thallium have been identified.

## 2. Environmental Characteristics

Compounds of gallium, indium, and, in particular, thallium can cause terrestrial environmental impacts; however, the elements are relatively rare and large releases are unlikely. Thallium compounds are on the Community Right to Know List. None of these elements, by themselves, have any known global environmental effects.

## 3. Toxicity

Gallium and indium compounds are moderately toxic, and thallium compounds are highly toxic. Respiratory system damage can result from inhalation of indium compounds.

## D. CONCLUSIONS AND RECOMMENDATIONS

Of the Group III elements, only aluminum and, possibly, boron can be considered. The remaining elements are rare and, in some cases, toxic. There is little evidence of fire suppression capabilities due to inherent characteristics of Group III elements outside of their use in flame retardants, where the action appears to be primarily physical. The borazoles and boroxoles could provide an interesting skeleton for attachment of fire suppressant groups such as difluorobromomethyl ( $-\text{CF}_2\text{Br}$ ) and 2-bromo-2,2-difluoroethoxy ( $-\text{OCH}_2\text{CF}_2\text{Br}$ ); however, significant additional work is needed to examine the toxicity, syntheses, and stability of such compounds.



## SECTION VIII

### COMPOUNDS OF GROUP IV ELEMENTS

This group contains carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). Carbon compounds are too numerous to include as a separate group and are best discussed in the context of the heteroatom contained. The Group IV elements range from strictly nonmetallic carbon to metallic lead.

#### A. SILICON COMPOUNDS

As a result of the conclusions from this report, a major report on the chemistry, toxicity, syntheses, and properties of silicon compounds as potential fire suppressants has been written (Reference 85).

##### 1. Chemistry and Fire Suppression

Silicon forms fewer compounds with fewer functional groups than does carbon. This is due primarily to two reasons. First, due to the larger atomic radius of silicon compared to carbon, the strengths of the Si-Si bond (214 kJ/mol, 51 kcal/mol) and Si-H bond (318 kJ/mol, 76 kcal/mol) are lower than those of the C-C bond (347 kJ/mol, 83 kcal/mol) and C-H bond (414 kJ/mol, 99 kcal/mol). Second, silicon does not form stable  $p\pi \leftrightarrow p\pi$  (Figure 8) bonds (e.g.,  $O=C=O$  exists, but  $O=Si=O$  does not).



Figure 8.  $p\pi \leftrightarrow p\pi$  Bonding.

When bonded to atoms containing lone pairs of electrons (in particular, the halogens, oxygen, and nitrogen), “back donation” of these lone pairs (which have primarily

p atomic orbital character) into empty d orbitals on the silicon atom gives some double bond character. This additional bonding is often referred to as “ $p\pi \rightarrow d\pi$  bonding” (Figure 9). Thus, while bonds between silicon and atoms containing no lone pairs are weaker than the corresponding carbon bonds, the reverse is true for bonds involving atoms with lone pairs (e.g., halogens, oxygen, and nitrogen).

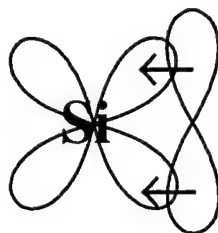


Figure 9.  $p\pi \rightarrow d\pi$  Bonding in Si-X (X = Halogen) and Si-O Bonds.

Silicon most commonly exhibits a +4 oxidation state with a coordination number of four. Although most compounds are tetravalent and tetrahedral at the silicon atom, silicon d orbitals have energies that make possible the formation of pentavalent or hexavalent states. Thus, hydrolysis of silicon halides (e.g., Reaction 14, where X represents a halogen atom and R is any substituent) is much more rapid than that of carbon, which has a maximum valence of four, even though both reactions are thermodynamically favorable. The hydrolytic cleavage (Reaction 14) of the Si-halogen bond may proceed through a pentavalent transition state, which greatly lowers the activation energy and makes the reaction kinetically favorable (Figure 10).

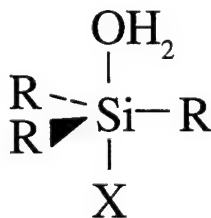


Figure 10. Pentavalent Transition State Proposed for Hydrolysis of a Silicon Halide.

Among the silicon compounds, only two (but large) classes have been identified as those that should receive consideration for development of fire suppression agents: the silanes, which may contain Si-Si bonds, and the siloxanes that contain Si-O-Si linkages (Figure 11). All inorganic silicates are solids, and the silicon halides are highly susceptible to hydrolysis, rendering them toxic. Thus, these latter two families of compounds are not promising candidates as fire suppressants, though for different reasons.

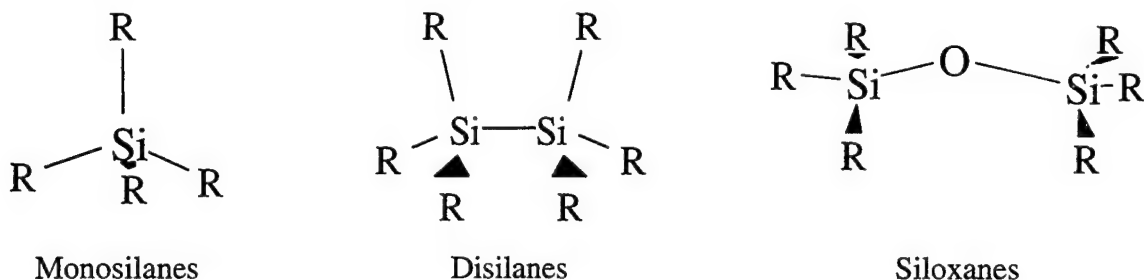


Figure 11. Silanes and Siloxanes.

Silicon derivatives are highly promising. Some silicon compounds are known to have relatively short atmospheric lifetimes. Many materials containing silicon-bromide and silicon-chloride bonds are highly effective fire extinguishants. The peak in the flammability curve for silicon tetrachloride ( $\text{SiCl}_4$ ) is 9.9 percent by volume for a premixed *n*-heptane flame (Reference 86). This value is a little lower than that of 11.5 percent for carbon tetrachloride,  $\text{CCl}_4$ , found in the same study; however, it indicates no special fire suppression ability for silicon.  $\text{SiCl}_4$  decreases the burning velocities of stoichiometric *n*-hexane/air mixtures (Reference 87). Unfortunately, however, silicon halides readily hydrolyze and are, therefore, toxic. On the other hand, bromine substitution on alkyl groups contained in silicon and siloxane compounds, is likely to provide effective extinguishment without the problem of hydrolysis. Moreover, most siloxanes have low toxicities.

Polysiloxanes have been used in fire protection agent mixtures with phosphates and other materials; however, the amounts used are sufficiently small that the extinguishment capability may be due to the phosphate (References 91, 88). Self-extinguishing polymers containing silicon are, of course, well known (see for example, Reference 89).

## 2. Environmental Characteristics

Silicon is a common terrestrial element and significant terrestrial environmental impacts due only to silicon itself are unlikely.

Based on a rather detailed and lengthy analyses and estimations reported elsewhere (Reference 85), silicon compounds containing bromocarbon substituents should have atmospheric lifetimes on the order of days and ODPs of less than 0.02. Since these materials are expected to have only one primary commercial application (fire suppression), it is likely that their use would not be significantly restricted due to their global environmental effects.

## 3. Toxicity

Compounds containing silicon directly bonded to halogens are, as expected, highly toxic owing to rapid hydrolysis of the silicon-halogen bond. Subacute toxicity testing on a limited number of industrial chemicals indicates that stable silane derivatives have a low toxicity (Reference 82). For example, rats exposed for 6 hours to 8000 ppm of tetramethylsilane  $[\text{Si}(\text{CH}_3)_4]$  showed no toxic signs, and organs were found to be normal on autopsy. A number of siloxanes are used industrially and most appear to have a low toxicity.

## B. OTHER GROUP IV COMPOUNDS

### 1. Chemistry and Fire Suppression

On a mole basis, lead tetraacetate (Pb) is a highly effective extinguishant for ethanol flames when introduced as an aerosol (Reference 56), and, in fact, was one of the most effective metal compounds found. Lead 2,4-propanedioate(1-) [lead acetylacetonate,  $\text{Pb}(\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3)_2$ ] is also relatively effective.

Ammonium hexachlorostannate(IV)  $[(\text{NH}_4)_2\text{SnCl}_6]$  is a strong catalyst of free radical recombination rates in fuel-rich, premixed  $\text{H}_2/\text{O}_2/\text{N}_2$  flames (Reference 68). The homogeneous gas-phase Reactions 15 and 16 are proposed.



Tin(IV) chloride ( $\text{SnCl}_4$ ), like many other metal chlorides, is a flame inhibitor, comparing roughly with titanium(IV) chloride ( $\text{TiCl}_4$ ) and antimony(III) chloride ( $\text{SbCl}_3$ ) (Reference 90). A fire extinguishant mixture containing a small amount of dibutyltin dioctoate  $[(\text{C}_4\text{H}_9)_2\text{Sn}(\text{C}_8\text{H}_{15}\text{O}_2)_2]$  has been reported (Reference 91).

$\text{GeCl}_4$  and  $\text{SnCl}_4$  (like  $\text{SiCl}_4$ ) decrease the burning velocities of stoichiometric *n*-hexane/air mixtures with the effectiveness increasing with molecular weight (Reference 87).

## 2. Environmental Characteristics

Lead compounds present terrestrial environmental hazards and are on the Community Right to Know List. Tin compounds are known to be hazardous to marine organisms. The terrestrial environmental impact of germanium compounds has not been well assessed, probably due to their low availability.

## 3. Toxicity

Germanium compounds have a relatively low toxicity. Experimental  $\text{LD}_{50}$  values are around 500 to 5000 mg/kg for ingestion (Reference 92). Tin compounds have a variable toxicity; however, many are poisonous and can exhibit moderate toxicity on inhalation. The high toxicity of lead compounds is well known and does not need further discussion here.

## C. CONCLUSIONS AND RECOMMENDATIONS

Germanium is too costly to be considered, and tin and lead are environmentally unacceptable. Thus, excluding carbon compounds discussed throughout this report, only silicon compounds provide promising candidates for halon replacements among the Group IV elements.

Silicon-based materials containing bromine are expected to provide good fire extinguishment, comparable to the halons. The atmospheric lifetimes, ODPs, and GWPs should be sufficiently low that the compounds are environmentally acceptable. To avoid toxicity and stability problems, it is essential that halogen atoms (fluorine, chlorine, bromine, and iodine) should not be attached directly to the silicon atom. Such molecules are highly susceptible to hydrolysis in moist air with the formation of hydrogen halides. Compounds containing haloalkyl

groups such as  $\text{-CF}_2\text{Br}$ , where halogen atoms are attached only to carbon and do not hydrolyze rapidly, can be considered. It is important to keep the number of hydrogen atoms as low as possible to decrease flammability. With these criteria in mind, a review of the properties and syntheses of silicon compounds has been completed with an emphasis on those that either contain bromine or could be used as skeletons for attachment of suitable bromine-containing groups.

Two groups of silicon compounds are found to be of particular interest—silanes (which are analogous to the carbon-containing alkanes) and siloxanes (which contain one or more  $\text{Si-O-Si}$  groups). Alkoxy derivatives are particularly promising because of their enhanced stability and the potential for increased degradation in the troposphere owing to enhanced abstraction of hydrogen atoms adjacent to the oxygen atom by tropospheric hydroxyl free radicals.

The major uncertainties with silicon compounds are the manufacturability and the toxicity. It is known that the toxicities of many of the parent compounds are very low; however, bromination may increase the toxicity. In general, fluorination is expected to improve volatility, fire suppression performance, and, in some cases, toxicity. However, compounds containing fluorine on a carbon atom adjacent to silicon are inherently unstable, and this may be a major problem associated with synthesis and use.

## SECTION IX

### COMPOUNDS OF GROUP V ELEMENTS

Group V includes the elements nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi).

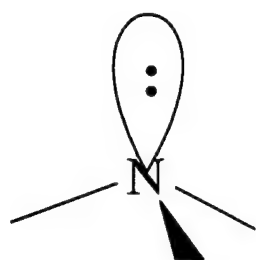
#### A. NITROGEN

##### 1. Chemistry and Fire Suppression

Nitrogen can form both  $\sigma$  bonds—formed from the end-on overlap of  $sp$ ,  $sp^2$ , or  $sp^3$  hybrid orbitals (Figure 6)—or  $p\pi \leftrightarrow p\pi$  bonds involving sideways overlap of  $p$  orbitals (Figure 8). The N-N single  $\sigma$  bond is relatively weak compared to the C-C bond; the single bond energy for  $H_3C-CH_3$  is 350 kJ/mol (84 kcal/mol), while that of  $H_2N-NH_2$  is only 160 kJ/mol (38 kcal/mole) (Reference 93). The simultaneous formation of both a  $\sigma$  and a  $\pi$  bond gives  $=N=N=$  compounds, where “=” denotes a  $\sigma + \pi$  double bond.

The most common nitrogen compounds are the pyramidal compounds containing three single ( $\sigma$ ) covalent bonds to nitrogen with a lone pair of electrons at the vertex and bent compounds containing double-bonded nitrogen with a lone pair. Including the lone pair the former compounds such as  $:NH_3$  are often said to be “tetrahedral,” and the latter, as in  $R_2C=N=N$  (R is any group), are termed “trigonal planar” (Figure 12). Other geometries are also possible (e.g., linear as in  $:N \equiv N:$  and tetrahedral as in the ammonium ion  $NR_4^+$  and in nitroxide compounds containing the  $R_3N \rightarrow O$  grouping); however, these are of little interest here.

Fluorinated derivatives of carboxylic acid hydrazides having the general formula  $RC(O)N(CF_2X)NHCNCF_2X$ , where R is a hydrocarbon and X is fluorine, perfluoroalkyl, or  $\omega$ -hydroperfluoroalkyl are reported to be nonflammable and, in some cases, to act as fire extinguishants (Reference 94). The compounds can be prepared by reaction of an aldehyde with a polyfluoroazoalkane (Reaction 17). One example of a fire extinguishing compound of this type is N,N'-bis(perfluoropropyl)-N-butyrohydrazide (VIII).

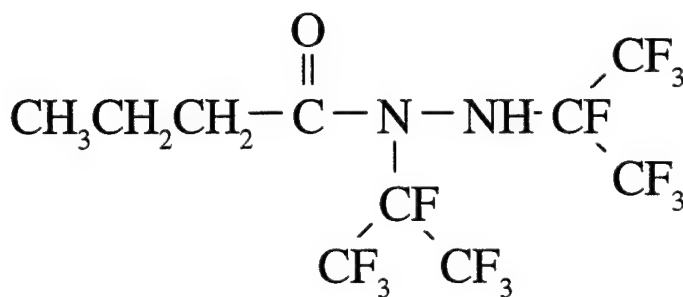


tetrahedral (pyramidal)



trigonal planar (bent)

Figure 12. Common Geometries of Nitrogen Compounds.



VIII

Researchers at the National Industrial Research Institute of Nagoya have evaluated fluoroalkylamines, with an emphasis on perfluoroalkyl derivatives, as fire suppressants (Reference 95). The inhibition effect of several bromine-free polyfluoroalkylamines including  $\text{N}(\text{CF}_3\text{CF}_2)_3$ ,  $\text{N}(\text{CF}_3)_2(\text{CF}_2\text{CF}_3)$ ,  $\text{N}(\text{CF}_3)_2(\text{CF}_2\text{CHF}_2)$ , and  $\text{N}(\text{CF}_3)_2(\text{CF}=\text{CF}_2)$  on flame propagation has been measured by determining the laminar burning velocity for a mixture of 9.5 percent methane, 90.0 percent air, and 0.5 percent inhibitor, at an initial temperature of 25 °C (77 °F) and a pressure of 760 Torr. All of the fluoroalkylamines inhibited flame propagation less than Halon 1301 but more than HFC-227ea ( $\text{CH}_3\text{CHF}_2\text{CF}_3$ ). Calculations showed that the inhibition effect of the fluoroalkylamines was caused not only by physical factors, but also by a chemical process in which fluorinated species capture combustion chain carriers ( $\bullet\text{H}$ ,  $\bullet\text{O}$ , and  $\bullet\text{OH}$ ) to form stable HF molecules. The inhibition efficiencies of fluoroalkylamines were found to be higher than those



of fluoroalkanes since fluoroalkylamine decomposes to reactive fluoroalkyl radicals in the lower temperature region of each flame (Reference 96). *Ab initio* molecular orbital calculations indicate that fire suppression by perfluoromethylamines is due, in part, to reactions of the trifluoromethyl radical, which can be easily released from perfluoroalkyl-amine by dissociation of C-N bonds (Reference 97). The proposed Reactions 18 through 20 are similar to those proposed for bromine in the case of the halons (Reference 85). It should be noted, however, that others have found no evidence for participation of  $\bullet\text{CF}_3$  in flame inhibition (Reference 98).



## 2. Environmental Characteristics

There is nothing inherent in nitrogen that leads to a terrestrial environmental impact; however, specific compounds may cause environmental problems. Thus, any analysis of terrestrial environmental threat must be made on the specific compound involved.

Like the parent compound ammonia, trialkylamines such as trimethylamine  $[\text{N}(\text{CH}_3)_3]$  are tetrahedral with a lone-pair of electrons occupying one tetrahedral site (Figure 13). This lone pair causes the amine to be basic, which does two things. First, it causes simple alkyl amines to have a relatively high toxicity. Second, the atmospheric lifetime of simple alkyl amines is very short since they are water soluble (or, at least, partially water soluble) and highly susceptible to rainout.\*

Fluorine substitution greatly changes the geometry and the physical properties of alkyl amines. Due to electron withdrawal by the attached perfluoroalkyl groups, the lone pair in tris(perfluoroalkyl)amines is effectively removed. Tris(trifluoromethyl)amine  $[\text{N}(\text{CF}_3)_3]$ , for example, is essentially nonbasic (and, therefore, insoluble in water) and is planar rather than

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\*Due to the presence of hydrogen atoms on the alkyl groups, they can also react with stratospheric hydroxyl free radicals.

tetrahedral (Figure 13). Thus, both toxicity and rainout are greatly reduced. In fact, tris(perfluoroalkylamines) are likely to have little if any significant tropospheric removal, and their atmospheric lifetimes are believed to be very long.

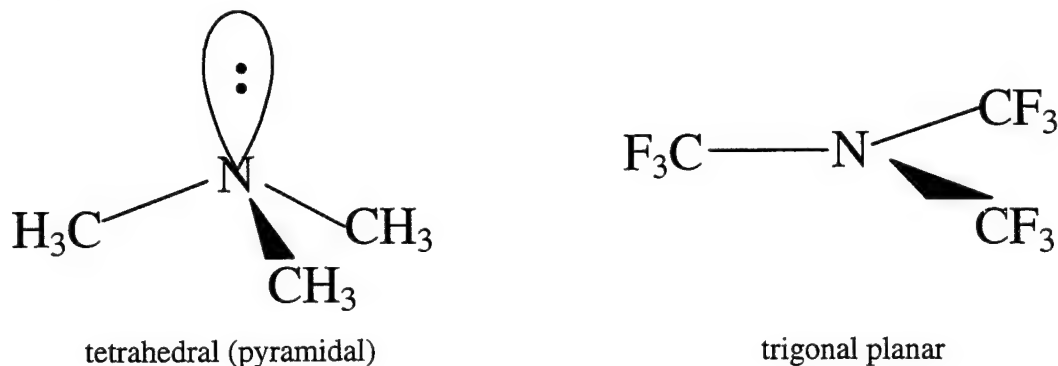


Figure 13. Methylamine and Tris(trifluoromethyl)amine.

When hydrogen atoms are present on both an amine alkyl group and on the nitrogen, C-H abstraction by tropospheric hydroxyl free radicals ( $\bullet\text{OH}$ ) tends to occur in preference to or in competition with N-H abstraction. The presence of a nitrogen atom decreases the C-H bond strength making it more susceptible reaction with hydroxyl free radicals. Thus, the bond energies for C-H in  $\text{CH}_4$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ , and  $(\text{CH}_3)_3\text{N}$  are, respectively, 435, 391, 364, and 352 kJ/mol (104, 93.3, 87, and 84 kcal/mol) (Reference 99). As would be expected from these data, a nitrogen atom alpha to a C-H bond significantly increases the reaction rate constant for hydrogen abstraction by hydroxyl free radicals. This can be seen in the rate constants in Table 6 (Reference 100), which compares rate constants between amines and structurally similar hydrocarbons. For this limited set of data, the amine rate constants are 23 to 65 times larger than the hydrocarbon rate constants. The calculated atmospheric lifetimes  $t_{1/e}$  for the amines in Table 6 are less than 1 day based on their reactions with tropospheric hydroxyl free radicals only.

TABLE 6. RATE CONSTANTS FOR REACTIONS OF AMINES AND HYDROCARBONS WITH HYDROXYL FREE RADICALS.

Compound	$k_{OH}^1$ , cm <sup>3</sup> /molecule-s	Compound	$k_{OH}^1$ , cm <sup>3</sup> /molecule-s
CH <sub>3</sub> CH <sub>3</sub>	$3.40 \times 10^{-13}$	CH <sub>3</sub> NH <sub>2</sub>	$2.20 \times 10^{-11}$
(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	$1.37 \times 10^{-12}$	(CH <sub>3</sub> ) <sub>2</sub> NH	$6.54 \times 10^{-11}$
(CH <sub>3</sub> ) <sub>3</sub> CH	$2.67 \times 10^{-12}$	(CH <sub>3</sub> ) <sub>3</sub> N	$6.09 \times 10^{-11}$

The atmospheric environmental parameters of some HFAs are given in Table 7;\* however, the reliability of the numbers is uncertain. They may be estimates. The atmospheric lifetime for dimethyl(pentafluoroethyl)amine [(CH<sub>3</sub>)<sub>2</sub>NC<sub>2</sub>F<sub>5</sub>] is unusually large, and it is probably in error. It may be that the compound is the fully fluorinated material (CF<sub>3</sub>)<sub>2</sub>NC<sub>2</sub>F<sub>5</sub> or that the lifetime should have been 250 days rather than 250 years. The  $t_{1/e}$  value for (CF<sub>3</sub>)<sub>2</sub>NCH<sub>3</sub> of 0.28 years is of particular interest since replacement of one of the fluorine atoms by bromine is likely to reduce this to about 0.028 years due to enhanced photolysis (Reference 85). A very small amount of data indicates that for bromine-containing compounds, each 10 years increase in atmospheric lifetime increases the ODP by approximately 2 (Reference 85). Thus, for an atmospheric lifetime of 0.028, methyl(trifluoromethyl)(bromodifluoromethyl)amine [(CBrF<sub>2</sub>)(CF<sub>3</sub>)NCH<sub>3</sub>] would have an ODP of 0.006. This analysis indicates that hydrobromofluoroamines, which are expected to have a fire extinguishment capability similar to that of the halons, are candidates with a low environmental impact.

### 3. Toxicity

Many simple nitrogen compounds are toxic upon inhalation (e.g., simple amines and nitrogen oxides); however, it is impossible to make any generalizations about the toxicities of nitrogen-containing compounds. In fact, many nitrogen compounds are required in human metabolism (e.g., the amino acids).

\*Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December, 1995. (Unpublished)

TABLE 7. ATMOSPHERIC CHARACTERISTICS OF SOME HFAs.

Compound	Lifetime, years	GWP based on CFC-11 <sup>a</sup>	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
$(\text{CH}_3)_2\text{NC}_2\text{F}_5$	<sup>b</sup> 250	4.3	4973	6527	5349
$(\text{CF}_3)_2\text{NCHFCH}_3$	2.98	0.06	930	287	90
$(\text{CF}_3)_2\text{NCF}_2\text{CHF}_2$	2.98	0.06	839	257	80
$(\text{CF}_3)_2\text{NCH}_3$	0.28	0.007	98	30	9
$(\text{CF}_3)_2\text{NCF}_2\text{CF}_2\text{H}$	2.10	0.01	141	43	13

<sup>a</sup>CFC-11 is trichlorofluoromethane,  $\text{CCl}_3\text{F}$ .

<sup>b</sup>This value is highly suspect (see text).

As noted earlier, fluorine-substitution of alkyl amines increases atmospheric lifetime (a bad effect) but decreases the polarity and toxicity (a good effect). It is difficult to determine the correct balance between these two features, one desirable and the other undesirable. The acute inhalation toxicity of some HFAs are give in Table 8.\* These lower bounds do not cause any concern; however, measurements at higher concentrations are needed. In addition to these, the  $\text{LC}_{\text{LO}}$  for mouse inhalation has been reported as  $500 \text{ mg/m}^3$  (0.01 percent) for 2,2,2-trifluoroethylamine  $[(\text{CF}_3\text{CH}_2)\text{NH}_2]$ , CAS No. = 753-90-2]. This value appears rather low; however, note that this compound contains hydrogen atoms rather than fluoroalkyl groups directly bonded to the nitrogen. Fluoroalkyl groups are expected to decrease the toxicity significantly (by reducing the basicity of the amine).

## B. PHOSPHORUS

Based, in part, on this AAWG evaluation, a detailed report on the application of phosphorus compounds, with an emphasis on phosphorus nitrides, has been written

\*Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December, 1995. (Unpublished)

TABLE 8. ACUTE INHALATION TOXICITY OF HFAs.

Compound	LC <sub>50</sub> , mg/L	Molecular weight	LC <sub>50</sub> , %
<sup>a</sup> (CF <sub>3</sub> ) <sub>2</sub> NCH <sub>3</sub>	>20	113.99	>0.43
<sup>a</sup> (CF <sub>3</sub> ) <sub>2</sub> NCF <sub>2</sub> CF <sub>2</sub> H	>20	253.04	>0.19
<sup>a</sup> (CF <sub>3</sub> ) <sub>2</sub> NCFHCF <sub>3</sub>	>20	253.04	>0.19
<sup>a</sup> (CF <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CF <sub>3</sub>	>20	235.05	>0.21
<sup>b</sup> (CF <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CF <sub>2</sub> H	>20	217.06	>0.23
<sup>b</sup> (CF <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>3</sub>	>20	181.08	>0.27

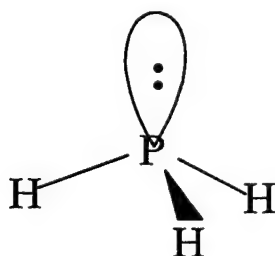
<sup>a</sup>3-Hour rat.<sup>b</sup>4-Hour rat.

(Reference 101). Some laboratory studies on flame suppression by these compounds have also been carried out (Reference 102).

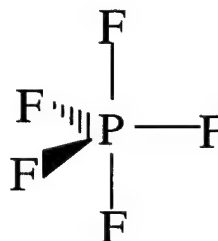
### 1. Chemistry and Fire Suppression

Phosphorus exhibits four common oxidation states in compounds:  $\pm 3$  and  $\pm 5$ .

This is not to say that other oxidation states may not occur, but that many of the most common phosphorus compounds exhibit one of these oxidation numbers. The simplest phosphorus compounds are those containing tricoordinate phosphorus(III) as in phosphine (PH<sub>3</sub>) and derivatives thereof or pentacoordinate phosphorus(V) as in phosphorus pentafluoride (PF<sub>5</sub>) (Figure 14).



phosphine: tetrahedral (pyramidal)



phosphorus pentafluoride: trigonal bipyramidal

Figure 14. Common Phosphorus Geometries.

Until relatively recently, compounds in which there are phosphorus  $p\pi \leftrightarrow p\pi$  bonds (Figure 8) were rare and extremely unstable. Today, a large number of compounds containing

phosphorus  $p\pi \leftrightarrow p\pi$  bonds have been prepared (Reference 103); however, they are generally less stable than compounds containing, e.g., nitrogen  $p\pi \leftrightarrow p\pi$  bonds.  $R\ddot{P}=\ddot{P}R$  compounds are difficult to prepare and must often be stabilized by bulky R groups.

Unlike nitrogen, the first member of the Group V elements, phosphorus has energetically available d orbitals and can form multiple bonds involving  $p\pi \leftrightarrow d\pi$  bonding (where phosphorus and the attached atom each donate one electron to the bond, Figure 9) as well as pentavalent species such as  $PF_5$  (Figure 14), which contains  $sp^3d$  hybrid orbitals.  $p\pi \rightarrow d\pi$  "back bonding" (where the atom attached to phosphorus donates both electrons to the bond, Figure 9) can occur when phosphorus is bonded to an atom such as oxygen containing one or more lone pairs of electrons. For example, the phosphine oxides are usually written as  $O=PR_3$  to denote the double bond character in the PO bond due to the presence of  $p\pi \rightarrow d\pi$  bonding, whereas the amine oxides are written as  $O-NR_3$  since  $p\pi \rightarrow d\pi$  bonding is not possible for these compounds.



Figure 15.  $p\pi \rightarrow d\pi$  Bonding.

Phosphorus forms a large number of oxyacids, many of which contain more than one phosphorus atom (usually with P-O-P linkages). Figure 16 shows the primary single-phosphorus oxyacids of phosphorus—phosphoric acid,  $OP(OH)_3$  (also known as orthophosphoric acid); phosphonic acid,  $OPH(OH)_2$  (originally called phosphorous acid, a name now reserved for the hypothetical acid  $P(OH)_3$ ); and phosphinic acid,  $OPH_2(OH)$  (originally called hypophosphorous acid, a name now used for the hypothetical alternative structure  $PH(OH)_2$ ). Phosphoric acid is triprotic, phosphonic acid is diprotic, and hypophosphonic acid is monoprotic. Phosphoric acid forms three phosphate esters— $O=P(OH)_2(OR)$ ,  $O=P(OH)(OR)_2$ , and  $O=P(OR)_3$ . Phosphonic acid gives two phosphonate esters— $O=PH(OH)(OR)$  and  $O=PH(OR)_2$ .

These are often written as the “phosphite” forms  $P(OH)_2(OR)$  and  $P(OH)(OR)_2$ , where they can be considered as derivatives of the hypothetical phosphorous acid,  $P(OH)_3$ ; however, these two esters almost certainly exist only in the phosphonate forms with  $P=O$  and  $P-H$  bonds. A series of very common compounds includes the trialkyl and triaryl “phosphites.” These materials appear to exist as two interconvertable forms— $P(OR)_3$ , which can be considered as derived from the hypothetical acid  $P(OH)_3$  and  $O=PR(OR)_2$ , which can be considered as derived from phosphonic acid. In most cases, the stable compounds have the phosphonate structure with a  $P=O$  bond. For historical reasons, however, the compounds are still most often named as phosphites and given the structure  $P(OR)_3$  rather than being named as phosphonates, with the structure  $O=PR(OR)_2$ .

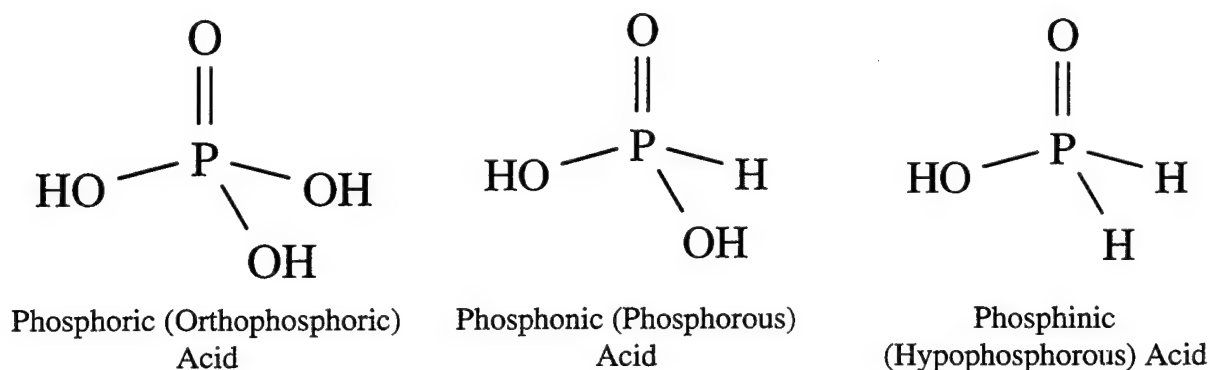


Figure 16. Principal Oxyacids of Phosphorus.

Phosphorus derivatives, such as  $O=P(R)_3$ , where “R” represents alkyl, alkoxy, aryl, and/or aryloxy groups, have been used to prepare flame and heat resistant polymers. The materials may be incorporated directly into polymers when the “R” groups contain appropriate functions. For example, the presence of OH groups allow the formation of polyesters (Reference 104) and halogen substituents permit the formation of ether linkages (Reference 105). Phosphite and phosphonium esters of bromoalkyl and bromoalkenyl alcohols have been incorporated into fire resistant plastics and monomers (References 106, 107). The compounds include  $P(O)(CH_2BrCHBrCH_2O)_3$ ,  $P(OCH_2CBr=CHBr)_3$ ,  $ClP(O)(OCH_2CBr=CHBr)_2$ ,  $CH_2=CHC(O)OCH_2CH_2OP(O)(OCH_2CBr=CHBr)_2$ .

Aromatic esters of phosphoric acids [e.g., diphenylmono(o-xylenyl)phosphate,  $O=P(OC_6H_5)_2(OCH_2C_6H_4CH_3)$ ] (Reference 108) and haloalkyl esters of phosphoric acids

(Reference 109) have been used in fire extinguishants for Class D (metal) fires. Aqueous solutions of  $\beta$ -hydroperfluoroalkyl phosphinic acids, having the general formula  $\text{CF}_3(\text{CF}_2)_n\text{CHFCF}_2\text{P}(\text{O})\text{H}(\text{OH})$ , and  $\beta$ -hydroperfluoroalkyl phosphinic acids, having the formula  $\text{CF}_3(\text{CF}_2)_n\text{CHFCF}_2\text{P}(\text{O})(\text{OH})_2$ , and their salts are reported to serve as fire extinguishants with particular applicability to Class B fires (Reference 110). Mixtures of halocarbons with organophosphate compounds (e.g., trimethylphosphate ester) have been claimed as fire extinguishants (Reference 111). Of particular interest is that  $(\text{CH}_3\text{O})_3\text{PO}$  contains no halogen atoms but exhibits an effect on flame velocity almost as great as  $\text{PCl}_3$ ,  $\text{PBr}_3$ , and related compounds (Reference 112).

A very large number of compounds containing phosphorus-nitrogen bonds have been prepared, and extensive compilations of physical property data are available (Reference 113). Very recently, some of these materials have been shown to be highly effective fire extinguishing agents (Reference 114). The most common of these materials, known as phosphazenes or phosphonitriles, contain alternating phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The phosphazenes are usually cyclic, but may also be polymeric (References 115-117). Linear phosphorus nitrides are also known and are often, but by no means always, polymers whose exact structures have not been fully characterized. Examples of a 6-member cyclic ring and a 4-member linear chain are shown in Figure 17.

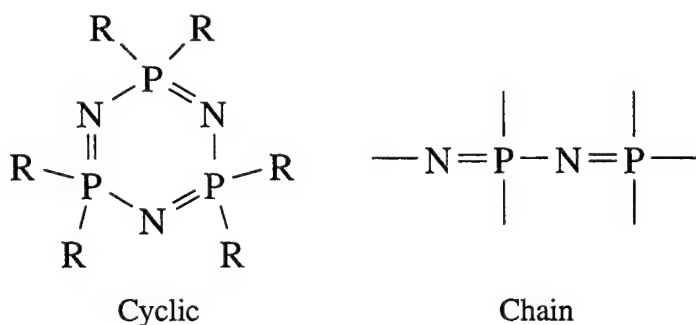
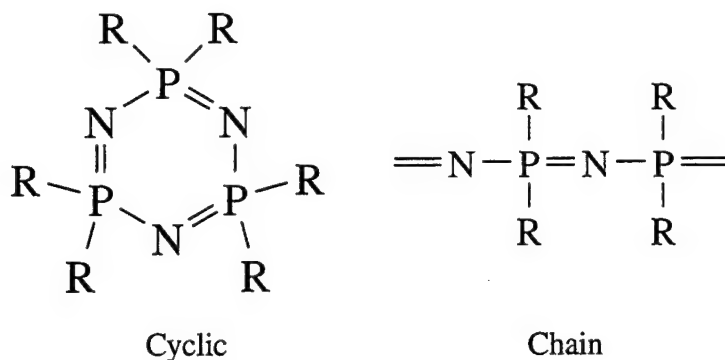


Figure 17. Phosphorus Nitride Structures.

The phosphorus nitrides are known to be highly effective as fire extinguishing agents (Reference 114). These materials exist as two groups—cyclic compounds containing a ring backbone (usually with alternating phosphorus and nitrogen atoms) and linear compounds,

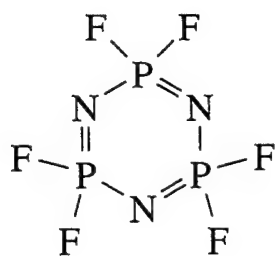


which have a linear chain backbone (but which also may contain cyclic substituents along the chain). The latter are often polymers whose exact structures have not been fully characterized. Examples are shown below for a six-member cyclic ring and for a four-member chain.

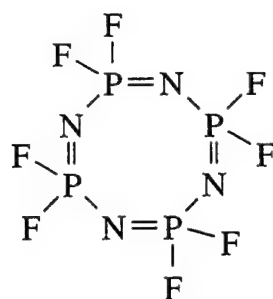


The backbones may contain substituents including but not limited to the halogens fluorine (F), chlorine (Cl), bromine (Br), and iodine (I); imino groups ( $=\text{NH}$ ); alkyl and substituted alkyl groups; aryl and substituted aryl groups; and alkoxides. Alkyl groups are groups containing only carbon and hydrogen atoms such as methyl ( $-\text{CH}_3$ ), ethyl ( $-\text{CH}_2\text{CH}_3$ ), *n*-propyl ( $-\text{CH}_2\text{CH}_2\text{CH}_3$ ), and *iso*-propyl ( $-\text{CH}(\text{CH}_3)_2$ ). Substituted alkyl groups are alkyl groups in which one or more of the hydrogen (H) atoms have been replaced by other atoms or groups. Examples are  $-\text{CH}_2\text{F}$ ,  $-\text{CHF}_2$ , and  $-\text{CF}_3$ . Aryl groups are groups containing only carbon and hydrogen atoms in “aromatic” rings. The most common of these is the phenyl group,  $-\text{C}_6\text{H}_5$ . Substituted aryl groups have one or more of the hydrogen atoms replaced by some other substituent. An example is perfluorophenyl,  $-\text{C}_6\text{F}_5$ . Alkoxide groups have the structure  $-\text{OR}$ , where R is an alkyl or a substituted alkyl group.

Fluorinated cyclic compounds include the trimers and tetramers  $\text{P}_3\text{N}_3\text{F}_6$  (IX) and  $\text{P}_4\text{N}_4\text{F}_8$  (X), and, in general, compounds having a formula  $(\text{PNF}_2)_n$ , where “n” is 2 or greater.



IX



X

Some impure mixtures of cyclic phosphorus nitrides exhibit cup-burner extinguishment concentrations as low as 0.3 percent (compared with average values of 2.9 percent for Halon 1301 and 3.2 percent for Halon 1211). Purified compounds have higher cup-burner values; however, the concentrations found are still well below those determined for Halons 1301 and 1211 (Table 9, Reference 114). Moreover, laboratory scale streaming tests have shown extinguishment times for phosphorus nitrides that are considerably shorter than those determined for Halon 1211.

The cyclic compound  $P_3N_3F_6$  is particularly interesting. Though the highly purified material is a solid, it exhibits a significant vapor pressure, even at low temperatures (Figure 18). Note that at  $0^\circ\text{C}$ , the vapor pressure of approximately 50 torr corresponds to a concentration at sea level of 14 percent, compared with the extinguishing concentration of approximately 1 percent (Table 9).

Unfortunately, however, the fluorinated phosphazenes apparently hydrolyze sufficiently fast that the toxicity is unacceptable (*vide infra*). For that reason, there is an increasing interest in the application of polyfluoroalkoxyphosphazenes, such as tris(4,4,4,3,3,2,2-heptafluoropropoxy)-tris(2,2,2-trifluoroethoxy)cyclotriphosphazene (XI), as fire suppressants. Many of these compounds are liquid and there is some evidence that the toxicity may be acceptable. A number of these materials have been evaluated as lubricants (Reference 118).

TABLE 9. CUP BURNER EXTINGUISHMENT CONCENTRATIONS WITH  
N-HEPTANE FUEL FOR PHOSPHORUS NITRIDE COMPOUNDS.

Compound	Cup Burner Extinguishing Concentration, %
$P_3N_3F_6$	1.12
	1.03
	1.18
	1.11
	0.94
Avg.	$1.08 \pm 0.07$
$P_3N_3ClF_5$	0.93
	0.86
	0.99
	0.86
Avg.	$0.91 \pm 0.02$
$P_3N_3Cl_2F_4$	1.11
	0.90
	0.85
	0.97
Avg.	$0.96 \pm 0.08$

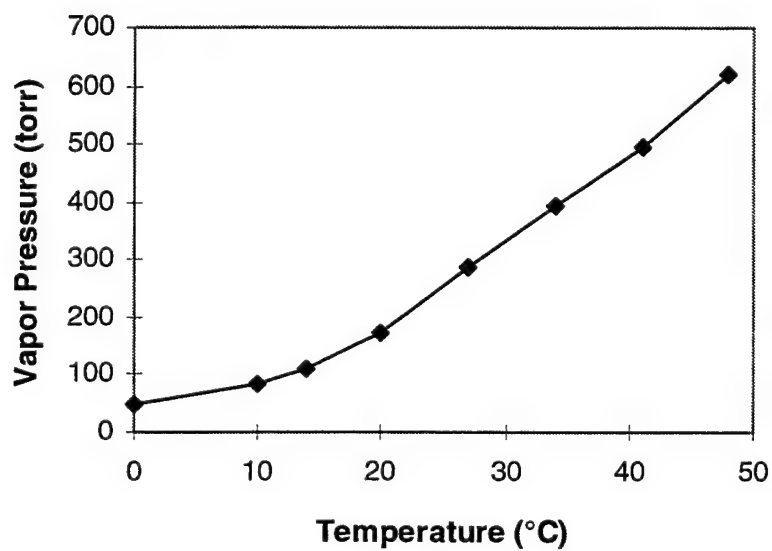
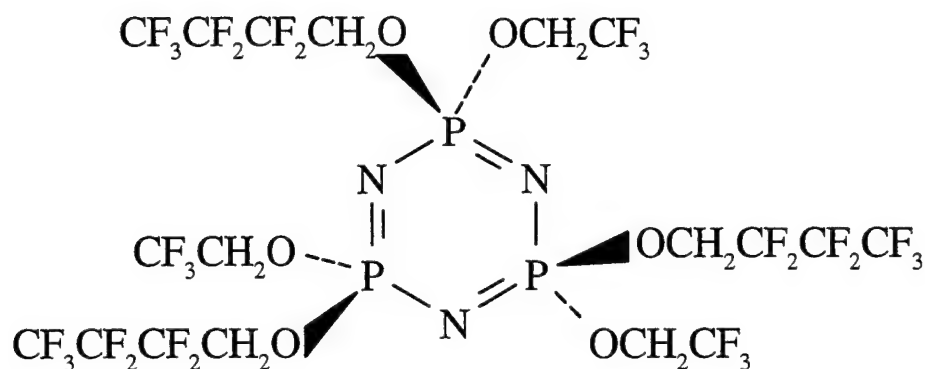


Figure 18. Vapor Pressure Curve for  $P_3N_3F_6$ .



XI

Red phosphorus has been used as a fire retardant for plastics. By itself, red phosphorus tends to increase carbon monoxide formation when used as a fire retardant for plastics; however, the addition of magnesium hydroxide to red phosphorus decreases both carbon monoxide and smoke (Reference 119). Red phosphorus by itself does not cause formation of a carbonaceous residue when used as a fire retardant for plastics. In combination with magnesium hydroxide, however, a char layer is formed.

## 2. Environmental Characteristics

Phosphorus is a common constituent of soils and is unlikely, in itself, to pose any terrestrial environmental impact. In large amounts, phosphates can cause eutrophication of bodies of water. There are no known mechanisms for global environmental impacts from any of the phosphorus compounds of interest here.

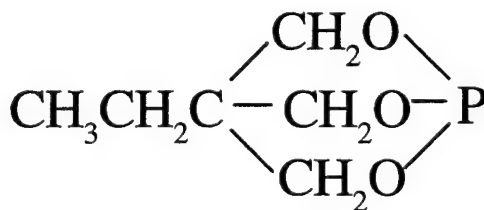
## 3. Toxicity

Of particular interest here is that extensive toxicity evaluations, including acute toxicity tests, inhalation, and skin kinetic studies, and 21-day repeated inhalation and dermal exposure testing have been carried out on an alkoxycyclotriphosphazene proposed as a hydraulic fluid (Reference 120). The test data indicate no toxicity to test animals from the phosphazene

fluid. The data also indicate that the fluid is poorly absorbed into the body by any route and appears to produce little or no effect when artificially introduced into the body.

One concern is that a number of phosphorus compounds (particularly phosphate esters) are cholinesterase inhibitors. Among these are poisonous insecticides such as parathion and methyl parathion and chemical warfare agents such as GB (Sarin) and VX (Reference 121). Some compounds with P-N bonds are cholinesterase inhibitors. One example is octamethylpyrophosphoramidate,  $[(CH_3)_2N]_2P(O)OP(O)[N(CH_3)_2]_2$ , which is a poison by numerous routes and has a 4-hour rat inhalation  $LC_{50}$  of  $8 \text{ mg/m}^3$  (Reference 122). The concern is with not only the neat phosphorus compounds that might be used as agents, but with decomposition products from flame and hot-surface contacts.

Subacute toxicity testing of industrial organic phosphorus compounds has shown that 1,1,1-tris(hydroxymethyl)propane bicyclic phosphite (XII), a solid, with a melting point of  $56^\circ\text{C}$  ( $133^\circ\text{F}$ ) showed that this compound has an unexpectedly high toxicity, with a marked CNS activity (Reference 82). All rats died with a 4-hour exposure to 10 ppm. The same study showed no toxic signs for fifteen 6-hour exposures to tributyl phosphite  $[P(OCH_2CH_2CH_2CH_3)_3]$ , a liquid with a boiling point of  $125$  to  $127^\circ\text{C}$  ( $257$  to  $261^\circ\text{F}$ ) at 15 Torr.



XII

As part of the AAWG work, 3M Company performed toxicity testing on the hexafluorocyclotriphosphazene ( $P_3N_3F_6$ ).<sup>\*</sup> This compound, with a purity of greater than 99.9 percent, was screened for acute inhalation toxicity in two rodent species. A single rat was

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<sup>\*</sup>The official International Union of Pure and Applied Chemistry (IUPAC) name is 2,2,4,4,6,6-hexafluoro-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine (CAS No. 15599-91-4); however, for convenience, the more common name hexafluorocyclotriphosphazene is used here.

exposed to test material at a nominal concentration of 1000 ppm for 10 min. Within 3 minutes, the animal showed signs of hyperactivity and within 5 minutes had difficulty breathing and appeared moribund. The rat died 10 minutes after inhalation; necropsy revealed deep red, fluid-filled lungs. Mice exposed to the test material at a nominal concentration of 1000 ppm for 20 minutes exhibited symptomology identical to the rat. Death occurred 20 minutes after initiation of exposure; no necropsy was performed.

Death appeared to be due to pulmonary edema caused by the breakdown of the blood-air barrier. Other agents that cause this effect include hydrohalogen gases (including HF), alkylating agents, and several fluoroalkenes. However, the high purity of the test material (>99.9 percent) indicates that the toxic response was likely attributable to the test compound and not an impurity. The rapid onset of symptoms and death suggest that the eventual 4-hour rat inhalation  $LC_{50}$  for hexafluorocyclotriphosphazene would be much lower than 1000 ppm.

### C. OTHER GROUP V COMPOUNDS

#### 1. Chemistry and Fire Suppression

Antimony appears to exhibit a synergistic effect with bromine-containing compounds (Reference 123) and has been widely used as a synergist for polymer retardants (Reference 124). Most commonly antimony(III) oxide (antimony trioxide,  $Sb_2O_3$ ) is used; however, antimony(V) oxide (antimony pentoxide,  $Sb_2O_5$ ) and sodium antimonate ( $NaSbO_3$ ) are also used. The effectiveness appears to decrease in the order  $Sb_2O_3 > Sb_2O_5 > NaSbO_3$ . The materials are usually employed in conjunction with chlorinated and brominated compounds where they enhance the flame suppression (References 125 and 126). Though the details are unknown, mechanism is assumed to involve formation of antimony(III) halide ( $SbX_3$ ), which may then remove flame free radicals in the same way that halons do. For example, the proposed initial reaction is shown in Reaction 21, with subsequent steps being those in Reactions 24 through 26.



Like many other chlorides, antimony(III) chloride ( $\text{SbCl}_3$ ) is a flame inhibitor, comparing roughly with titanium(IV) chloride ( $\text{TiCl}_4$ ) and Tin(IV) chloride ( $\text{SnCl}_4$ ) (Reference 90).

2. Environmental Characteristics

Arsenic and antimony compounds are on the Community Right to Know List.

3. Toxicity

Arsenic and most antimony compounds are poisons by ingestion. Bismuth compounds, on the other hand, are among the less toxic of the heavy metal compounds.

D. CONCLUSIONS AND RECOMMENDATIONS

Hydrobromofluoroamines and, possibly (if work elsewhere on fire extinguishment is correct) hydrofluoroamines are promising candidates as halon replacements. With a proper balance of fluorine and hydrogen, the hydrobromofluoroamines should have low atmospheric lifetimes, acceptable ODPs, and, it is hoped, acceptable toxicities. Of particular importance is that the expected physical properties make these compounds promising as total-flood agents.

Phosphorus compounds, in particular phosphorus nitrides, offer high promise as Halon 1211 substitutes in streaming applications. Due to their low volatilities, the compounds offer less promise as Halon 1301 substitutes. Of particular interest are the fluoroalkoxy-substituted cyclotriphosphazenes; however, a number of other classes of compounds also offer potential.

## SECTION X

### COMPOUNDS OF GROUP VI ELEMENTS

This group contains oxygen, sulfur, selenium, tellurium, and polonium. Oxygen-containing halocarbons (e.g., ethers) have long been considered as potential replacements for halons.

#### A. OXYGEN

##### 1. Chemistry and Fire Suppression

The principal oxidation state for oxygen is -2. Most oxygen compounds are two-coordinate (e.g., water,  $\text{H}_2\text{O}$ , with  $s \leftrightarrow sp^3$   $\sigma$  bonds) or are monocoordinate with double bond (e.g., carbon dioxide,  $\text{CO}_2$ , with  $sp \leftrightarrow sp^3 + p\pi \leftrightarrow p\pi$  bonding). In both cases, the oxygen atom has two lone pairs of electrons (Figure 19).



Figure 19. Common Oxygen Coordinations.

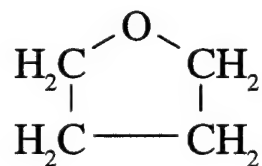
There is nothing in the chemistry of oxygen that implies significant activity as a chemically active fire suppressant. The primary reason for considering oxygen is to provide a short atmospheric lifetime to allow the use of bromine within the molecule. There are three families of oxygen compounds that could allow a short atmospheric lifetime (*vide infra*): alcohols, ethers, and carbonyl compounds. In each case, bromine must be present, and in each case, fluorination is probably needed to obtain a low hydrogen content and reduce flammability.

**Alcohols** are oxygenated compounds in which a hydroxyl (-OH) group is attached to a hydrocarbon skeleton. The structure of the alcohol molecule is similar to that of the water



molecule (Figure 19). In fact, alcohol molecules can be considered as derived from a water molecule by replacing one of the hydrogen atoms with an organic group. Examples of alcohols are methanol ( $\text{CH}_3\text{-O-H}$ ), ethanol ( $\text{CH}_3\text{CH}_2\text{-O-H}$ ), and ethylene glycol [ $\text{H-O-CH}_2\text{CH}_2\text{-O-H}$ ]. Various fluorinated compounds have been synthesized by replacing one or more of the hydrogen atoms with fluorine. Little, if any, fire suppression work has been reported for alcohols.

**Ethers**, like alcohols, can be considered as "derivatives" of water, except that both hydrogen atoms are replaced by hydrocarbon groups. For example, dimethylether is  $\text{CH}_3\text{-O-CH}_3$ . Cyclic ethers, for example tetrahydrofuran,  $\text{C}_4\text{H}_8\text{O}$  (XIII), are also possible. The alkyl groups can be halogen substituted to give, for example, the perfluoroether (PFE or FE) hexafluorodimethyl ether ( $\text{CF}_3\text{OCF}_3$ ). The most promising compounds would be partially fluorinated ethers containing hydrogen adjacent to the nitrogen atom (to enhance hydroxyl free radical abstraction and, thereby shorten the atmospheric lifetime, *vide infra*) and bromine to provide fire suppression. The resulting hydrobromofluoroethers (HBFEs) would be based on the hydrofluoroethers (HFE), about which some chemistry is known.



XIII

A relatively large amount of work has gone into the perfluoroethers as replacements for refrigerants and other ozone-depleting chemicals. Of greater interest here, however, are the ethers that are only partially substituted by fluorine—the HFEs. Such compounds have a significantly shorter atmospheric lifetime than do the perfluoroethers. In fact, PFEs are believed to have atmospheric lifetimes similar to those of the perfluorocarbons (PFCs or FCs).

Two fluorinated materials announced as substitutes for ozone-depleting cleaning agents (Reference 127) are the HFEs methyl perfluorobutyl ether ( $\text{C}_4\text{F}_9\text{OCH}_3$ ) and ethyl

perfluorobutyl ether ( $C_4F_9OC_2H_5$ ). The compositions and properties are given in Table 10.\*

More recently, a number of additional HFEs have been announced as refrigerants (Table 11).†

TABLE 10. HFEs ANNOUNCED AS CLEANING AGENT SUBSTITUTES.

Property	$C_4F_9OCH_3$	$C_4F_9OC_2H_5$
Halocarbon number	HFE-449s1	HFE-569sf2
Boiling point, °C	60	73
Melting point, °C	-135	-117
Flash point, °C	None	None
Flammability limits	None	None
Solubility of water at 25°C, ppm	95	92
Solubility in water at 25°C, ppm	<10	<10
Liquid density at 23°C, g/mL	1.50	1.43
Viscosity at 23°C, cp	0.4	0.4
Surface tension at 23°C, dynes/cm	13.6	13.6
Heat of vaporization, 23°C, kJ/kg	125.6	125.6
Specific heat, kJ/kg-K	1.172	1.214
ALC (Approximate Lethal Concentration)	>10%	>5%

\*Grenvell, M. W., Klin,, F. W., Owns, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995. (Unpublished)

†Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995. (Unpublished)

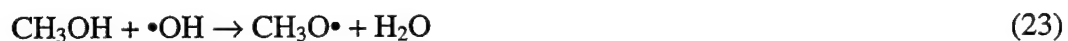
TABLE 11. PROPERTIES OF SOME HFEs.

Compound	Boiling point, °C	Liquid density, g/mL	Thermal conductivity, W/m-K	Specific heat, kJ/kg-K
CHF <sub>2</sub> OCH <sub>2</sub> CF <sub>3</sub>	29.0	1.391	0.1053	1.368
CHF <sub>2</sub> OCHFCF <sub>3</sub>	23.3	1.454	0.0943	1.286
CH <sub>3</sub> OCF <sub>2</sub> CHF <sub>2</sub>	37.2	1.288	0.1059	1.444
CH <sub>3</sub> OCF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	34.2	1.409	0.0753	1.246
CH <sub>3</sub> OCF(CF <sub>3</sub> ) <sub>2</sub>	29.9	1.420	0.0780	1.208
CF <sub>3</sub> CH <sub>2</sub> OCF <sub>2</sub> CF <sub>3</sub>	27.8	1.448	0.0801	1.269
CH <sub>3</sub> OCF <sub>2</sub> CF <sub>3</sub>	5.6	a	a	a

<sup>a</sup>Not available.

## 2. Environmental Characteristics

**Alcohols** containing hydrogen atoms can react with tropospheric hydroxyl free radicals. For a compound such as CH<sub>3</sub>OH, hydrogen atom abstraction by hydroxyl free radicals can occur from either the alkyl group (Reaction 22) or the hydroxyl group (Reaction 23). In general, abstraction by both pathways is observed, and the relative importance depends on the structure of the alcohol and the reaction temperature (Reference 100).



The addition of an OH group to a carbon atom containing a hydrogen atom greatly increases the reaction rate for abstraction of that hydrogen atom by hydroxyl free radical. This can be seen in the reaction rate constants for methane, CH<sub>4</sub>, of  $1.8 \times 10^{-14}$  cm<sup>3</sup>/molecule-s and methyl alcohol, CH<sub>3</sub>OH,  $1 \times 10^{-12}$  cm<sup>3</sup>/molecule-s (Reference 100).

A limited amount of information on atmospheric lifetimes and GWPs of fluorinated alcohols is available (Table 12).<sup>\*</sup> Insufficient details have been reported, however, to judge the reliability of the values given. The atmospheric parameters for (CH<sub>3</sub>)<sub>3</sub>COH in Table 12 appear to be incorrect. The atmospheric lifetime seems to be far too long. The rate constant for reaction of this compound with hydroxyl free radicals is approximately 1/5 that for reaction of (CH<sub>2</sub>)<sub>2</sub>CHOH (Reference 100), but the atmospheric lifetime is reported as 350 times higher for (CH<sub>3</sub>)<sub>3</sub>COH. The approximation method of Wuebbles and Connell (Reference 128), gives an estimated lifetime for (CH<sub>3</sub>)<sub>3</sub>COH of 131 days based on hydrogen abstraction alone. It may be that the paper cited contains a misprint of "years" for "days."

TABLE 12. ATMOSPHERIC ENVIRONMENTAL PARAMETERS FOR FLUORINATED ALCOHOLS.

Compound	Lifetime, years	GWP based on CFC-11	GWP based on carbon dioxide		
			20-year time horizon	100-year time horizon	500-year time horizon
<sup>a</sup> (CH <sub>2</sub> ) <sub>2</sub> CHOH	0.32	0.005	79	24	8
<sup>a,b</sup> (CH <sub>3</sub> ) <sub>3</sub> COH	113.13	2.29	5543	6144	3232
CF <sub>3</sub> CH <sub>2</sub> OH	0.16	0.006	86	26	8
CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OH	0.57	0.01	135	25	13
<sup>c</sup> (CF <sub>2</sub> ) <sub>4</sub> CH(OH)	2.18	0.03	519	159	50
CF <sub>3</sub> CH <sub>2</sub> OH	0.55	0.01	123	38	12
(CF <sub>3</sub> ) <sub>2</sub> CHOH	2.60	0.04	637	195	61
CF <sub>3</sub> CF <sub>2</sub> CH <sub>2</sub> OH	0.60	0.01	145	44	14

<sup>a</sup>Non-fluorinated alcohol included for comparison.

<sup>b</sup>This value is highly suspect (see text).

<sup>c</sup>The formula indicates that this is a cyclopentanol, although the structure was not given.

<sup>\*</sup>Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December, 1995. (Unpublished)

Rainout can also be an important physical removal process for polar compounds such as alcohols. However, little is known at this time about the reaction rates and how they might affect the atmospheric lifetimes of alcohols.

**Ethers** have a very low polarity due to the oxygen atom; however, there is little indication that this decreases atmospheric lifetime due to rainout. The atmospheric lifetimes of PFEs are particularly long. The presence of hydrogen atoms makes hydrogen atom abstraction possible by hydroxyl free radicals. Moreover, the presence of an ether linkage increases the rate of this reaction. An oxygen group alpha to the position from which hydrogen abstraction occurs should increase the rate constant by a factor of  $e^{631/T}$ , and moving a  $CF_3$  group out of this position should increase the rate constant by an additional factor of  $e^{771/T}$  (Reference 129). Thus, for  $T = 265$  K, the rate constant should increase by a factor of  $e^{1410/T} = e^{5.32} = 204$ . The rate constant for an HFE would, therefore, be approximately 200 times larger and the atmospheric lifetime would be approximately 1/100 of the value of the non-ether, but fluorinated, parent compound. Indeed, data for a number of ethers show rate constants approximately  $10^2$  larger than similar hydrocarbons (Reference 100).

Lifetimes reported for HFEs vary widely. For example, pentafluorodimethyl ether,  $CHF_2OCF_3$  (HFE-125) and bis(difluoromethyl)ether,  $CHF_2OCHF_2$  (HFE-134) are reported to have atmospheric lifetimes of 82 years and 8 years (Reference 130). The value for HFE-125 is particularly long. On the other hand, a recent report lists HFEs with atmospheric lifetimes as low as 0.3 years.\*† As expected, the atmospheric lifetimes decrease as the number of hydrogen atoms increase.

### 3. Toxicity

**Alcohols** exhibit a range of toxicities. Methanol, causes mild inebriation followed in about 10 to 20 hours by unconsciousness and cardiac depression; death may follow.

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\*Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995. (Unpublished)

†Grenvell, M. W., Klin., F. W., Owns, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995. (Unpublished)

Sublethal exposure may lead to blindness. The symptoms of ethanol are well known—decreased inhibitions and CNS depression are the first symptoms, followed by stupor, coma, and death at higher doses. Ethanol can be absorbed through the lungs and symptoms of intoxication observed at 1000 ppm. Ethylene glycol, the anti-freeze/antiboiling formulation in most automotive cooling systems, stimulates the CNS and then depresses it; potentially fatal kidney damage can occur.

The toxicity of higher molecular weight alcohols range from relatively low to moderate. 2-propanol ( $\text{CH}_3\text{CHOHCH}_3$ ) is a food additive. It can be an irritant and narcotic, but the toxicity is relatively low. Allyl alcohol ( $\text{CH}_2=\text{CHCH}_2\text{OH}$ ) is strongly irritating to eyes, mouth, and lungs. Deaths have been reported in laboratory animals but not humans (Reference 131). The following irritants—1-butanol ( $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$ ), 2-ethylhexanol ( $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$ ), and 1-pentanol ( $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$ )—have limited toxicity due to low vapor pressure. Most other higher molecular weight alcohols are also considered to be moderately toxic by ingestion or skin contact (Reference 132).

2-*tert*-Butoxyethanol [ $(\text{CH}_3)_3\text{COCH}_2\text{CH}_2\text{OH}$ ] has been shown to have similar hemolytic effects similar to those exhibited by 2-*n*-butoxyethanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ) in other studies, apparently increasing the fragility of red blood cells (Reference 82). The compound caused death in seven out of eight rats with a single 5-hour exposure to 2400 ppm. 2-Isopropoxyethanol [ $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{OH}$ ] appears to have somewhat less marked effects. Of particular interest is that tris(pentafluoroethyl)methanol [ $(\text{CF}_3)_3\text{COH}$ ] is a powerful uncoupler of oxidative phosphorylation, and caused death in rats with a 1-hour exposure at a concentration of 100 ppm. 1-Chloro-2-propanol [ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$ ] is an irritant and one out of four rats died following two 6-hour exposures to 1000 ppm.

**Ethers**, in a study of chemicals having industrial application, have been shown to universally cause CNS depression similar to that of diethyl ether (Reference 82). Bis(2-chloro-1-methylethyl)ether [ $\text{CH}_2\text{ClCH}(\text{CH}_3)\text{OCH}(\text{CH}_3)\text{CH}_2\text{Cl}$ ] is an irritant and causes death in rats with a single 5-hour exposure to a 700-ppm concentration. Overall, however, ethers have a relatively low toxicity in comparison to many other families of chemicals.

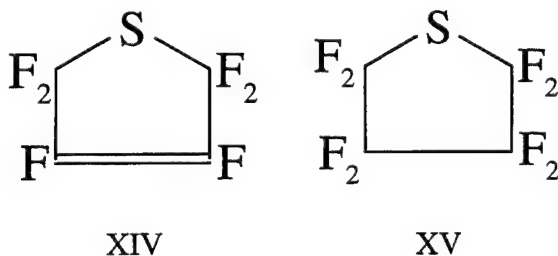
**Carbonyl compounds** exhibit a range of toxicities depending on whether carbonyl group is in an aldehyde, ketone, carboxylic acid, or ester. In a study of industrial chemicals at subacute levels, aldehydes have been shown to have anesthetic properties, but are not marked irritants (Reference 82). Unsaturated esters of saturated carboxylic acids, e.g., vinyl acetate  $[\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3]$  typically exhibit a low toxicity with high concentrations causing irritation and narcosis. Note, however, that many of these esters have such a low volatility that exposure concentrations were low. Chloroformates such as methylchloroformate  $[\text{CH}_3\text{OC}(\text{O})\text{Cl}]$  are highly toxic.

## B. SULFUR

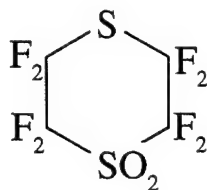
### 1. Chemistry and Fire Suppression

Sulfur hexafluoride ( $\text{SF}_6$ ) has long been considered as a fire extinguishant; however, the very high GWP makes this material unattractive.  $\text{SF}_6$ , presumably like other sulfur compounds, acts primarily as a PAA.  $\text{SF}_6$  has also been used in a fire extinguishant propellant (Reference 133) and as a fire extinguishant simulant (Reference 134). Ammonia derivatives of fluoroalkyl sulfocarboxylic acids, e.g.,  $\text{RCF}(\text{SO}_2\text{NH}_2)\text{C}(\text{NH}_2)(=\text{NH})$ , are surface active agents reported to enhance water as a fire extinguishant for Class B fires (Reference 135).

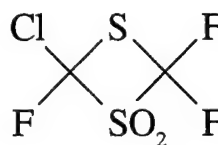
Hexafluoro-2,5-dihydrothiophene [(XIV), boiling point  $40^\circ\text{C}$  ( $104^\circ\text{F}$ )], prepared by reaction of sulfur with hexafluorocyclobutene, has been reported to extinguish flames (Reference 136). Perfluorothiolane [(XV), boiling point  $41^\circ\text{C}$  ( $106^\circ\text{F}$ )], prepared by reaction of tetrafluoroethene ( $\text{F}_2\text{C}=\text{CF}_2$ ) with sulfur in the presence of iodine also exhibits flame extinguishment (Reference 137). Neither heterocyclic sulfur compound is flammable.



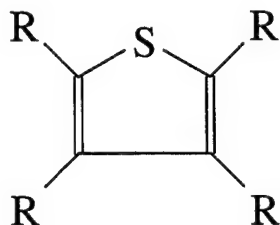
Polyfluorinated cyclic sulfones such as perfluoro-1,1-dioxo-1,4 dithiane [(XVI), melting point 65.5 to 66.3 °C (149.9 to 151.3 °F)] and 1,1-dioxo-2-chloro-2,4,4-trifluoro-1,3-dithietane [(XVII), boiling point 69 °C at 60 Torr pressure (149.9 to 151.3 °F) and  $n_D = 1.4527$ ] are nonflammable and are claimed to be generically useful as fire retardants and extinguishants (Reference 138). A number of related materials (XVIII, XIX, XX, where R represents polyfluoroalkyl groups) are also said to extinguish fires and to be useful as fire retardants and ingredients in fire extinguishing compositions (Reference 139).



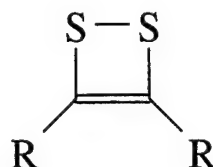
XVI



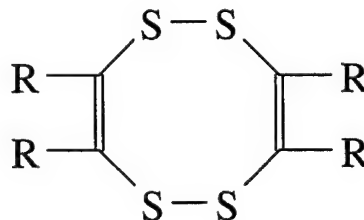
XVII



XVIII



XIX



XX

## 2. Environmental Characteristics

Sulfur compounds are so variable in environmental effects, depending on the structure, that a general assessment of the impact on the terrestrial environment cannot be made. Thus, for example, sulfates are a common component of soils. Global environmental impacts due to sulfur alone are not expected.

## 3. Toxicity

Because of their high reactivity, many sulfur compounds, particularly the oxides and mercaptans, are powerful lung irritants.



Sulfur hexafluoride ( $\text{SF}_6$ ) has a low toxicity; however, replacement of one of the fluorine atoms by a chlorine greatly increases toxicity, with deaths occurring in rats at a 1-hour exposure at 100 ppm (Reference 82).

Subchronic toxicity inhalation studies have been run on a series of liquid (haloalkyl)pentafluorosulfur(VI) compounds ( $\text{RSF}_5$ , where R is a normal alkyl chain with a terminal chlorine atom) (Reference 82). The results indicate that fluorination of the alkyl chain decreases toxicity (compare  $\text{ClCH}_2\text{CH}_2\text{SF}_5$  and  $\text{ClCF}_2\text{CF}_2\text{SF}_5$ ) and that toxicity decreased with increasing chain length (Table 13).

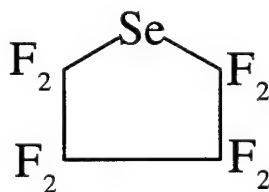
### C. OTHER GROUP VI COMPOUNDS

The remaining Group VI elements are selenium, tellurium, and polonium. The last element is radioactive.

#### 1. Chemistry and Fire Suppression

Selenium and tellurium are metalloids with some metallic properties. The formulas of many of their compounds are analogous to sulfur compounds; however, the properties of the compounds are usually distinct from those of the sulfur compounds.

Perfluoroselenolane [(XXI), boiling point  $62^\circ\text{C}$  ( $144^\circ\text{F}$ )], prepared by reaction of selenium with tetrafluoroethene ( $\text{F}_2\text{C}=\text{CF}_2$ ) in the presence of iodine, has been reported to extinguish flames (Reference 137).



XXI

TABLE 13. SUBCHRONIC TOXICITY OF (HALOALKYL)PENTAFLUOROSULFUR(IV) COMPOUNDS.

Compound	Formula	BP, °C (°F)	Exposure	Results
(2-Chloroethyl)pentafluorosulfur(VI)	$\text{Cl}(\text{CH}_2)_2\text{SF}_5$	92 (198)	4 rats, 200 ppm, 1 x 2-hr	tremors, convulsions, 1 died, organs normal
"			4 rats, 50 ppm, 20 x 6-hr	no toxic signs, organs normal
(2-Chlorotetrafluoroethyl)-pentafluorosulfur(VI)	$\text{Cl}(\text{CF}_2)_2\text{SF}_5$	46.5 (115.7)	4 rats, 5000 ppm, 1 x 3-hr	respiratory difficulty, gasping, convulsions, all died, lung edema, congested, liver congested
"			4 rats, 1000 ppm, 1 x 6-hr	respiratory difficulty, 3 died, lung edema
"			4 rats, 200 ppm, 15 x 6-hr	no toxic signs, organs normal
(4-Chlorooctafluorobutyl)-pentafluorosulfur(VI)	$\text{Cl}(\text{CF}_2)_4\text{SF}_5$	99 (210)	4 rats, 5000 ppm, 1 x 5-hr	no toxic signs, organs normal
"			3 rats, 500 ppm, 15 x 6-hr	no toxic signs, organs normal, slight lung congestion
(6-Chlorododecafluorohexyl)-pentafluorosulfur(VI)	$\text{Cl}(\text{CF}_2)_6\text{SF}_5$	143 (289)	4 rats, 2500 ppm, 2 x 5-hr	no toxic signs, organs normal
"			4 rats, 500 ppm, 13 x 6-hr	no toxic signs, organs normal

## 2. Environmental Characteristics

Selenium and tellurium are now used in relatively small amounts so that, for the most part, man-made compounds of these materials do not now constitute a major environmental problem. On the other hand, concentration of naturally occurring selenium due to water leaching and mining has caused some problems. Compounds of both selenium and tellurium would have an unacceptable terrestrial environmental impact if they found widespread use. With a half life of only 138 days, only extremely small amounts of polonium (from radioactive decay of radium) are found naturally.

## 3. Toxicity

Selenium and tellurium compounds are considered relatively toxic. Of course, radioactive polonium is highly toxic.

## D. CONCLUSIONS AND RECOMMENDATIONS

Of the Group VI elements, only oxygen and sulfur compounds offer reasonable potential as fire extinguishants. In the case of oxygen, other groups are needed to provide a chemical action agent (CAA), and this also be true for sulfur compounds. The most group providing chemical suppression action is bromine (see the following section). Thus, recommended for study are bromine-containing alcohols, ethers, and carbonyl compounds. In the case of the ethers, one or more hydrogen atoms would have to be present (preferably on the carbon atom adjacent to the ether oxygen) to obtain sufficiently short atmospheric lifetimes. In all cases, however, at least some fluorination would be needed to decrease flammability. Selenium, tellurium, and polonium cannot be considered owing to toxicity (polonium is radioactive).

## SECTION XI

### COMPOUNDS OF GROUP VII ELEMENTS

This group contains the halogens (fluorine, chlorine, bromine, iodine, and astatine). Halogens are contained in the most effective fire fighting agents, including Halon 1301. The earlier technology leading to these agents has been reviewed (Reference 140). It is these elements that cause the stratospheric ozone depletion, and potentially may cause global warming. Use of halogens to replace Halon 1301 must be in a form that does not contribute to ozone depletion or global warming. Much of the work developing replacements for Halon 1301 has revolved around innovative methods of providing halogen atoms while allowing breakdown of the constituent elements in the environment prior to its reaching the upper atmosphere.

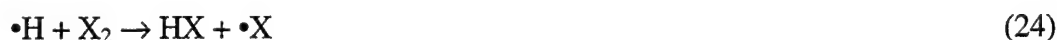
As noted earlier, physical action agents (PAAs) are those that operate primarily by heat absorption. Chemical action agents (CAAs) are those that operate primarily by chemical means—removal of flame free radicals. The chemical effect contribution to extinguishment by halocarbon PAAs is only 10 to 25 percent of the physical contribution (Reference 141). In general, halocarbon CAAs are much more effective extinguishants than are PAAs. Halons 1211 and 1301 are primarily CAAs. Work at the Naval Research Laboratory (NRL) indicates that Halon 1301 extinguishment of n-heptane in air is approximately 20 percent physical and 80 percent chemical (Reference 6). The analysis also indicates that about 25 percent of the extinguishment is due to the  $\text{CF}_3$  group and about 55 percent is due to the bromine. Though CAAs are more effective, they often have higher ODPs because they often contain bromine. One exception is trifluoroiodomethane,  $\text{CF}_3\text{I}$  (Reference 142), which is the only CAA being commercialized today.

Most halocarbons now being proposed as halon replacements require significantly higher concentrations than required for Halon 1301 and Halon 1211 and produce larger amounts of toxic and corrosive byproducts (e.g., hydrogen fluoride and, for chlorine-containing agents, hydrogen chloride) (Reference 143). Hydrogen fluoride formation is strongly influenced by the

mass flux of inhibitor into the flame sheet and by the time to extinguishment. Slow extinguishment due to use of lower concentrations of agent produces more byproducts.

#### A. HALOGENS AND FIRE EXTINGUISHMENT

Westbrook has proposed that a primary process for inhibition of hydrocarbon flames by halogen-containing species is a catalytic combination of hydrogen atoms by hydrogen halides (Reference 144). This is shown in Reactions 24 through 26, where X = F, Cl, Br, and I.



Here, "M" represents any third-body molecule that carries off energy from the recombination of halogen atoms ( $\bullet\text{X}$ ), giving an activated molecule,  $\text{M}^*$  (vibrational, rotational, and/or translational activation).

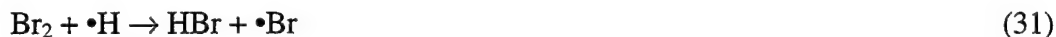
Since bond strength decreases in the order H-F, H-Cl, H-Br, and H-I, iodine and bromine are the most effective and fluorine and chlorine are the least effective. In fact, once H-F and, possibly, H-Cl are formed in Reaction 24, it is no longer available for participation in Reactions 25 and 26.

The net result of the catalytic cycle given by Reactions 24 through 26 is the combination of two hydrogen atoms to form relatively inactive diatomic hydrogen (Reaction 27).



In the case of inhibition by halocarbons, the initial reaction is probably a free-radical abstraction of a halogen atom by atomic hydrogen to form HX. The overall process is illustrated for Halon 1301,  $\text{CF}_3\text{Br}$ , in Reactions 28 through 31.





Note that the initial reaction, Reaction 28, could occur with other halogen atoms and even with hydrogen. This may explain why there appears to be a significant chemical contribution to flame extinguishment by  $\text{CH}_3\text{Cl}$ ,\* which could react as shown in Reaction 32 (in addition to reaction involving abstraction of the chlorine atom). Of course, this type of "extinguishment" occurs above the upper flammability region for any hydrogen-containing fuel.



Sensitivity analysis using modeling of methane combustion inhibition by bromine, indicates that methyl free radicals can also be involved in the catalytic cycle described in Reactions 33 through 35, which are similar to Reactions 29 through 31 (Reference 7).



In this case, the net result is the combination of a hydrogen atom and a methyl free radical to form methane (Reaction 36).



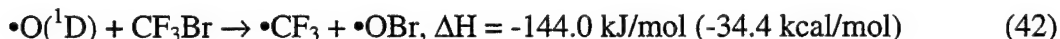
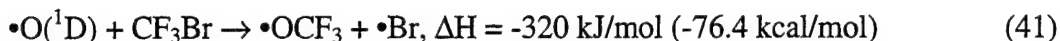
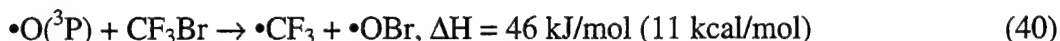
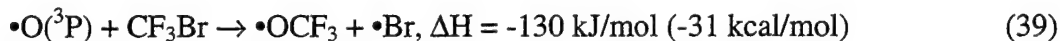
Other reactive species that promote combustion (e.g., oxygen atoms and hydroxyl free radicals) can also react with halogen-containing species. In fact, it has been proposed that removal of  $\bullet\text{OH}$  by halides (e.g., Reaction 37) is an important extinguishing mechanism since the depletion of  $\bullet\text{OH}$  slows the CO burnout (Reaction 38). Evidence for this mechanism in inhibition of methane/air flames by  $\text{CH}_3\text{Cl}$  has been reported (Reference 145).

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\*Brabson, G. D., Schiro, J., Patterson, R. A., Walters, E. A., and Tapscott, R. E., "Determination of Extinguishment Mechanisms," International CFC and Halon Alternatives Conference, Washington, DC, USA, 23-25 October, 1995. (Unpublished)



With the ground-state triplet ( $^3\text{P}$ ) and excited state singlet ( $^1\text{D}$ ) oxygen atoms, four reactions are possible (Reactions 39 through 42, Reference 146):



It has also been proposed that, at least in the case of methane combustion inhibition, a methane radical initially abstracts the bromide atom to give methyl bromide,  $\text{CH}_3\text{Br}$ , which then goes on to react with hydrogen atoms (Reactions 43 and 44, Reference 147).



Note that, in theory, bromine could be replaced by other halogens (fluorine, chlorine, and iodine) in Reactions 28 through 31. The ability to catalyze the reaction depends, however, on the strength of the hydrogen halide bond. Modeling experiments indicate little contribution to inhibition of methane combustion by  $\bullet\text{CF}_3$  (Reference 147).

Chlorinated and brominated flame retardants are widely used, particularly in the formulation of polymers (References 148 and 149). The materials are either incorporated into the polymer as a reactive monomer or are added to the polymer. Three types of chlorinated fire retardants are in use: aliphatics, aromatics, and cycloaliphatics. The most widely used chlorinated retardants are the aliphatic chlorocarbons. For optimum performance, compounds should not have too high a thermal stability, and the aromatics, such as decachlorodiphenyl ( $\text{C}_6\text{Cl}_5\text{-C}_6\text{Cl}_5$ ) have too high a stability for wide acceptance as flame retardants. It is found that a

chlorine content above 50 percent by weight is required for optimum performance. The most common brominated flame retardants are relatively high molecular weight aromatic systems such as decabromodiphenyloxide [ $C_6Br_5-O-C_6Br_5$ ] and tetrabromobisphenol A [ $C_6H_2Br_2(OH)-C(CH_3)_2-C_6H_2Br_2(OH)$ ]. Reactive molecules such as tetrabromobisphenol A and dibromostyrene ( $C_6H_3Br_2.CH=CH_2$ ) can act as monomeric building blocks for incorporation directly into a polymer. It is generally accepted that the flame extinguishment mechanism for the brominated retardants is similar to that of the halons; however, the retardants must break down or be released to effect extinguishment action. The mechanism of the chlorinated compounds is more uncertain since chlorine appears to have a relatively low efficiency in free-radical disruption. Most chlorinated and brominated retardants require a synergist such as antimony oxide ( $Sb_2O_3$ , the most common synergist), zinc borate [ $Zn_3(BO_3)_2$ ], zinc oxide ( $ZnO$ ), zinc stannate ( $ZnSnO_3$ ), and iron oxides ( $FeO$ ,  $Fe_2O_3$ ).

Although the flame retardant mechanism discussed above is a generally accepted vapor-phase mechanism, flash points and fire point of liquid systems as polymer models indicate that halogens act as flame retardants primarily by reducing the heat of combustion of the gases evolved during plastic decomposition, and not by retarding the gas-phase reaction kinetics (Reference 150). This has led to the proposal that halogens appear to act by increasing the mass of material that must volatilize per unit time in order to maintain a flammable composition in the gas phase.

The addition of dried molecular bromine ( $Br_2$ ) to a very well dried  $CO/O_2$  mixture causes a small decrease in flame velocity, only slightly stronger than the effect of the same amount of diatomic nitrogen ( $N_2$ ). Increasing  $H_2$  content, however, greatly increases the inhibiting effect of bromine (Reference 112). This may indicate that  $HBr$  is an essential component of the fire extinguishing mechanism. With hydrocarbon fuels, however, the effect of  $Br_2$  and  $Cl_2$  is more pronounced for fuels with low hydrogen content than for those with high hydrogen content.

## B. IODIDES

Organic iodides photolyze readily giving extremely short atmospheric lifetimes. The atmospheric chemistry of iodides has been reviewed (Reference 151). Trifluoromethyl iodide



(CF<sub>3</sub>I), which is as effective as Halon 1301, has an atmospheric lifetime of less than one day (Reference 152). A number of studies have proposed and/or tested fluoroiodides as halon replacements (References 153-157). Toxicological tests show a relatively low acute toxicity for CF<sub>3</sub>I, with a 4-hour rat ALC greater than 12.8 percent (Reference 158). The dog cardiac sensitization NOAEL is 0.2 percent; the Lowest Observed Adverse Effect Level (LOAEL) is 0.4†percent (Reference 159). Since the design concentration will be greater than 5 percent, the cardiotoxicity precludes the use of CF<sub>3</sub>I for total-flood applications in normally occupied areas. However, CF<sub>3</sub>I is still a highly promising replacement for unoccupied areas and in selected streaming applications.

Sprays of aqueous iodide salt solutions are superior to sprays of bromide salt solutions in extinguishing JP-8 fuel fires (Reference 63).

## C. HALOGEN-CONTAINING ALKENES

### 1. Chemistry and Fire Suppression

Hexafluoropropene (CF<sub>3</sub>CF=CF<sub>2</sub>, Reference 160), *cis*- and *trans*-1,2-dichloroethenes (CHCl=CHCl, Reference 161), n-perfluorobutylethene (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH=CH<sub>2</sub>, Reference 162), perchloroethene (CCl<sub>2</sub>=CCl<sub>2</sub>, Reference 163), trichloroethene (CCl<sub>2</sub>=CHCl, Reference 163), and hexabromo-2-butene (References 164, 165), and bromoalkenes in general (Reference 166)\* have been proposed for use in fire extinguishing agents and fire resistant treatments. A few bromoalkenes have been tested by cup burner (Reference 167, Table 14).

### 2. Environmental Characteristics

The bromoalkenes are rapidly destroyed by hydroxyl free radicals in the troposphere, and the polar-substituted bromocarbons are removed by rainout.

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\*Nimitz, J. S., Tapscott, R. E., and Skaggs, S. R., "Next-Generation High-Efficiency Halon Replacements," International CFC and Halon Alternatives Conference, Baltimore, Maryland, 3-5 December 1991. (Unpublished)

TABLE 14. BROMOALKENE EXTINGUISHING CONCENTRATIONS.

Formula	IUPAC Name	CAS Number	Ext. Conc., volume %
$\text{CH}_2=\text{CHCClFCBrF}_2$	4-Bromo-3-chloro-3,4,4-trifluorobutene	374-25-4	4.5
$\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$	4-Bromo-3,3,4,4-tetrafluorobutene	18599-22-9	3.5
$\text{CHBr}=\text{CHCF}_3$	1-Bromo-3,3,3-trifluoropropene		8.5
$\text{CH}_2=\text{CHCBrF}_2$	3-Bromo-3,3-difluoropropene	420-90-6	4.5
$\text{CH}_2=\text{CBrCF}_3$	2-Bromo-3,3,3-trifluoropropene	1514-82-5	2.6

### 3. Toxicity

Dichlorobutene and hexachlorobutadiene ( $\text{CCl}_2=\text{CClCCl}=\text{CCl}_2$ ), both four-carbon compounds, are highly toxic, producing severe kidney damage (Reference 82). Dichlorobutene, however, also causes severe lung irritation, and this effect predominates. On the other hand, chlorinated ethenes have a relatively low chronic toxicity, at least at low concentrations.

## D. HALOGEN-CONTAINING AROMATICS

### 1. Chemistry and Fire Suppression

The aromatics consist of cyclic carbon compounds formally containing alternating single and double bonds. Excluding some relatively rare organic ions, the simplest aromatic molecule is benzene ( $\text{C}_6\text{H}_6$ ). The structural formula for benzene (and other aromatics) can be written as two or more equivalent structures (e.g., structures XXII and XXIII for benzene in Figure 20), none of which adequately represents the actual structure due to delocalization of the  $\pi$  electrons over the ring. Structure XXIV in Figure 20 is a somewhat better representation for benzene.

It has been proposed that perfluorotoluene ( $\text{CF}_3\text{C}_6\text{F}_5$ , CAS No. 434-64-0) be examined for flame extinguishing properties (Reference 54). Bromine-containing aromatic compounds have been widely used as flame retardants for plastics (References 168 and 169), and aromatic materials may be directly brominated for use as flame retardants using antimony halides as catalysts (Reference 170). Little consideration has, however, been given to their use as fire

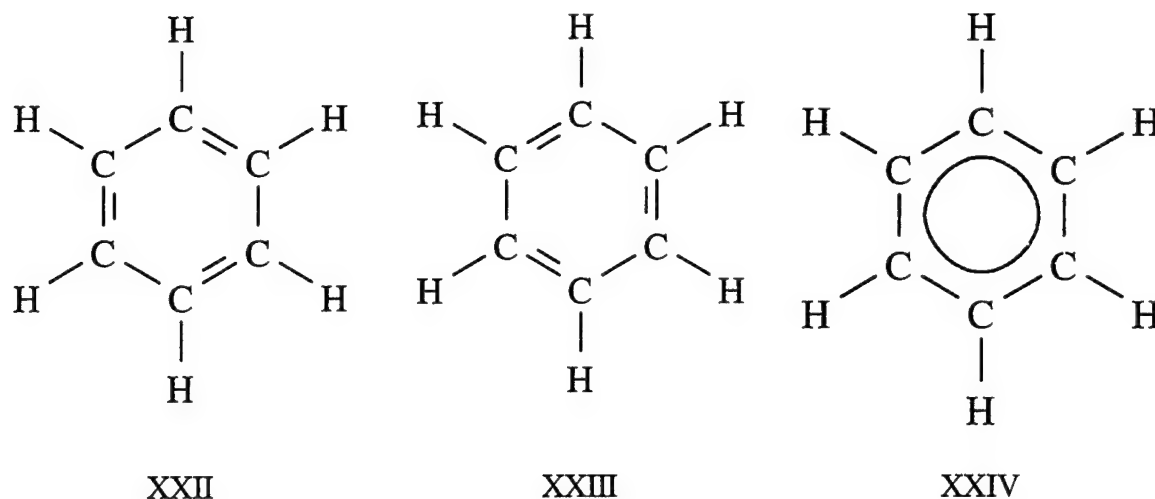


Figure 20. Graphical Structures for Benzene.

extinguishants. Many of the bromoaromatics used as plastic flame retardants are solids with reactive groups (for polymerization) and include compounds such as tetrabromobisphenol A [ $\text{CH}_3\text{C}(\text{C}_6\text{H}_2\text{Br}_2\text{OH})_2\text{CH}_3$ ], bis(tetrabromophthalamide) [ $(\text{C}_6\text{HBr}_2(\text{CONH}_2)_2)_2$ ], and dibromostyrene [ $(\text{C}_6\text{H}_3\text{Br}_2)\text{CH}=\text{CH}_2$ ].

Lower Flammability Limits (LFLs) of some halogenated aromatics that have been considered as anesthetics have been reported (Reference 171, Table 15).

## 2. Environmental Characteristics

Hydroxyl free radicals can add to the aromatics as well as to other unsaturated compounds. At about room temperature most  $\bullet\text{OH}$  radical reactions studied to date proceed by addition to the aromatic ring rather than by abstraction of a hydrogen atom. Rate constants for the reaction of hydroxyl free radicals with aromatic compounds are similar to those observed for the alkenes (Reference 100). Of particular interest is the 298 K rate constant of  $k_{\text{OH}} = 2.2 \times 10^{-13}$  and approximately  $3 \times 10^{-12} \text{ cm}^3/\text{molecule-s}$  observed for reactions with hexafluorobenzene ( $\text{C}_6\text{F}_6$ ) and *n*-propylpentafluorobenzene ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{F}_5$ ) (Reference 172). These compounds are closely related to some of the more promising tropodegradable aromatic candidates. The reaction rates for the nonfluorinated analogs are somewhat faster— $k_{\text{OH}} = 1.59 \times 10^{-12}$  and  $7.8 \times$

TABLE 15. LOWER FLAMMABILITY LIMITS OF SOME HALOARENES.

Compound	LFL, % by volume	
	Air	Oxygen
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	2.2	not reported
C <sub>6</sub> F <sub>6</sub>	not reported	5-6
C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub>	<10	8.3
C <sub>6</sub> F <sub>5</sub> Br	not reported	5.8

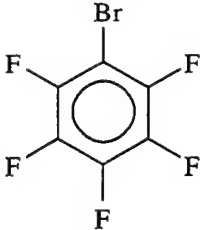
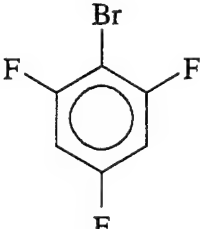
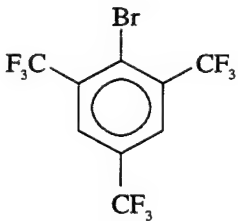
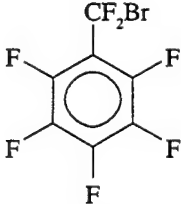
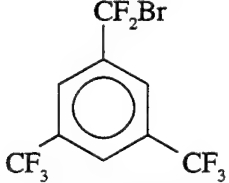
$10^{-12}$  cm<sup>3</sup>/molecule-s for benzene and *n*-propylbenzene (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, Reference 172).\*

Thus, fluorination of the aromatic ring decreases the reaction rate with •OH. One can calculate the first order rate constants for the two fluorinated compounds as  $k_1 = k_{OH} [\bullet OH]$ . This gives  $k_1 = 2.1 \times 10^{-7} \text{ s}^{-1}$  ( $t_{1/e} = 1/k_1 = 54$  days) for hexafluorobenzene and  $k_1 = 2.9 \times 10^{-6} \text{ s}^{-1}$  ( $t_{1/e} = 1/k_1 = 4$  days) for *n*-propylpentafluorobenzene.

One can use the method of Wuebbles and Connell (Reference 128) to estimate first-order rate constants and atmospheric lifetimes for a series of aromatic compounds of interest. The estimation method gives  $k_1 = 8 \times 10^{-8} \text{ s}^{-1}$ , ( $t_{1/e} = 145$  days) for hexafluorobenzene and  $k_1 = 3 \times 10^{-7} \text{ s}^{-1}$ , ( $t_{1/e} = 39$  days) for *n*-propylpentafluorobenzene. These rate constants are a little smaller than those determined from the experimental second-order rate constants above. For the *n*-propyl derivative, this may be due, in part, to the presence of some hydrogen atom abstraction from the alkyl group. Table 16 contains some estimations for other aromatic compounds having structures similar to those of interest as candidate fire suppressants. It is obvious from these values that aromatics have an excellent potential for environmental acceptability, even with bromine present.

\*In the case of the *n*-propyl derivative it is possible that some significant amount of reaction occurs by free-radical abstraction of hydrogen from the alkyl substituent.

TABLE 16. ESTIMATED FIRST-ORDER RATE CONSTANTS AND ATMOSPHERIC LIFETIMES FOR SOME BROMOFLUOROARENES.

Structure	Chemical name	$k_1, \text{sec}^{-1}$	Lifetime, days
	Bromopentafluorobenzene	$8.0 \times 10^{-8}$	145
	1-Bromo-2,4,6-trifluorobenzene	$9.8 \times 10^{-8}$	117
	1-Bromo-2,4,6-tris(trifluoromethyl)benzene	$4.4 \times 10^{-6}$	3
	(Bromodifluoromethyl)-pentafluorobenzene	$3.2 \times 10^{-6}$	4
	1-(Bromodifluoromethyl)-3,5-bis(trifluoromethyl)benzene	$4.9 \times 10^{-6}$	2.4

### 3. Toxicity

Pentafluorobenzene ( $\text{C}_6\text{HF}_5$ ) is a narcotic with an anesthetic concentration for cats of about 1.5 to 2.5 percent (Reference 82). With stepwise replacement of fluorine atoms by chlorine atoms, the anesthetic effects remain, and the compounds become cytotoxic with an effect on porphyrin metabolism (Table 17).

TABLE 17. SUBCHRONIC TOXICITY OF HALOGENATED BENZENES.

Compound	Formula	BP or MP, °C (°F)	Exposure	Results
Hexafluorobenzene	C <sub>6</sub> F <sub>6</sub>	liquid, BP: 80 (176)	8 rats, 1000 ppm, 4 x 6-hr	macrophages in lung; hyperplasia in spleen
"			8 rats, 500 ppm, 15 x 6-hr	weight gain retarded, organs, blood, urea normal
"			8 rats, 250 ppm, 15 x 6-hr	no toxic signs, organs normal
Chloropentafluorobenzene	C <sub>6</sub> ClF <sub>5</sub>	MP: 18.1 (64.6) BP: 116 (241)	8 rats, 1000 ppm, 4 x 6-hr	lethargy, lack of coordination, no porphyrinuria, organs normal
"			8 rats, 500 ppm, 15 x 6-hr	unresponsive, no porphyrinuria, organs normal
"			8 rats, 50 ppm, 15 x 6-hr	no toxic signs, organs normal
1,3-Dichlorotetra- fluorobenzene (approximately 5% of 1,2-isomer)	C <sub>6</sub> Cl <sub>2</sub> F <sub>4</sub>	liquid, BP: 156 (313)	4 rats, 3000 ppm, 1 x 30-min	eye irritation, nasal discharge, respiratory difficulty, light narcosis
"			8 rats, 1000 ppm, 4 x 6-hr	light narcosis with recovery overnight, increased urinary porphyrin products, kidney tubule damage
"			8 rats, 500 ppm, 15 x 6-hr	weight gain retarded, blood, urine normal slight kidney tubular lesions
"			8 rats, 100 ppm, 15 x 6-hr	no toxic signs, organs normal

TABLE 17. SUBCHRONIC TOXICITY OF HALOGENATED BENZENES (CONCLUDED).

Compound	Formula	BP or MP, °C (°F)	Exposure	Results
1,3,5-Trichloro-2,4,6-trifluorobenzene	C <sub>6</sub> Cl <sub>3</sub> F <sub>3</sub>	solid, MP: 50-60 (122- 140)	4 rats, 380 ppm, 2 x 6-hr	nose irritation, respiratory difficulty, narcosis, 2 rats died, increased urinary protein and porphyrin products, liver and kidney damage
"			8 rats, 83 ppm, 15 x 6-hr	no toxic signs, blood, urine normal, livers enlarged

#### E. CONCLUSIONS AND RECOMMENDATIONS

Bromoalkenes and bromoaromatics are expected to have exceedingly short atmospheric lifetimes to be seriously considered as halon replacements. Other bromine-containing compounds with short atmospheric lifetimes were discussed earlier in the sections covering nitrogen compounds (the hydrobromofluoroamines) and oxygen compounds (the hydrobromofluoroethers, bromine-containing carbonyl compounds, and bromine-containing alcohols).

## SECTION XII

### COMPOUNDS OF GROUP VIII ELEMENTS

Group VIII contains the noble gases helium, neon, argon, krypton, xenon, and radon. Radon is radioactive.

#### A. CHEMISTRY AND FIRE SUPPRESSION

All of the Group VIII gases can be used to reduce the oxygen level below that required for combustion. However, argon, given the designation IG-01 in the NFPA 2001 Standard (Reference 1), is the only Group VIII gas with a relatively widespread use. Argon is also a component in the blends IG-55 and IG-541.

Until the middle of this century, no compounds of the Group VIII elements were known. Today compounds of both xenon and krypton are known. The compounds tend to be relatively unstable and highly reactive. Moreover, no reports of inert gas compounds having been tested as fire extinguishants have been located.

#### B. ENVIRONMENTAL CHARACTERISTICS

With the exception of radon, which is radioactive, neither the pure noble gases nor their compounds are expected to exhibit any global environmental impact. Terrestrial environmental impacts for compounds of the noble gases is uncertain, but it is unlikely.

#### C. TOXICITY

Except for radon, the pure noble gases are nontoxic. Relatively few Group VIII compounds are known, and these tend to be toxic. However, more studies are needed in this area since the number of inert gas compounds is increasing.



#### D. CONCLUSIONS AND RECOMMENDATIONS

Compounds of the Group VIII elements offer a new field for investigation as fire extinguishants. These materials tend to be strong oxidizing agents and, admittedly, no mechanism is immediately obvious for any chemical action as a fire suppression. However, since these materials have not been investigated as fire suppressants, work in this area could lead to some interesting breakthroughs.

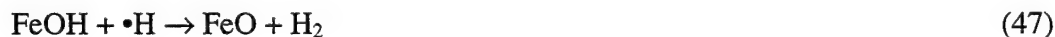
### SECTION XIII

#### TRANSITION METAL COMPOUNDS

##### A. CHEMISTRY AND FIRE SUPPRESSION

The transition metals group contains most of the metals. Transition metal compounds could provide highly effective fire extinguishing agents, and an extensive review of fire extinguishment by metal compounds has been written (Reference 55). For some time, it has been observed that certain metal compounds are very effective in extinguishing flames. For example, iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , may very well be one of the most effective extinguishing agents ever found (Reference 173). Moreover, chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , appears to be as much as two orders of magnitude more effective than the halons in inhibiting hydrocarbon flames (Reference 54). With  $\text{H}_2$  as a fuel, iron pentacarbonyl was less effective than with hydrocarbons (Reference 112). The latter paper proposes that the metals may react first with oxygen atoms or with OH radicals and in further steps with hydrogen atoms. It is also pointed out that the small particles obtained with metal compounds may influence their inhibiting effect.

Extinguishment by  $\text{Fe}(\text{CO})_5$  may involve the catalytic cycles involving Reactions 45 and 46 and/or Reactions 45 and 47.



Early work on inhibition by iron pentacarbonyl (Reference 174) has shown that

1. The burning velocity for stoichiometric mixtures of oxygen with methane, acetylene, and ethane is practically independent of pressure in the range 0.1 to several atmospheres. Below 0.1 atmospheres, the burning velocity increases with decreasing temperature.

2. The influence of  $\text{Fe}(\text{CO})_5$  on  $\text{CH}_4/\text{O}_2$  mixtures decreases with decreasing pressure.
3.  $\text{CH}_4$ -air mixtures are much more strongly inhibited than  $\text{CH}_4$ - $\text{O}_2$  mixtures.
4. There is some evidence that removal of OH free radicals by either homogeneous or heterogeneous reactions may be involved in flame inhibition by  $\text{Fe}(\text{CO})_5$ .

Work at NIST with iron pentacarbonyl has shown the following.\*

1. Inhibition of premixed methane/air flames by iron pentacarbonyl shows a significant dependence on the fuel/air equivalence ratio ( $\phi$ ). The agent is most effective on stoichiometric flames ( $\phi = 1$ ). The decrease in effectiveness is greatest for fuel-rich flames. Similar, but less dramatic, results are found for propane/air flames.
2. Incremental inhibition of premixed flames by iron pentacarbonyl decreases as the iron pentacarbonyl concentration increases. Additional inhibition by added agent is virtually nonexistent at higher concentrations (above approximately 100 ppm for premixed methane/air flames).

Transition metals (iron, chromium, manganese, etc.) are elements that contain incomplete d-block electronic shells in one or more of their compounds. The extinguishing ability of transition metal compounds may be due to these incomplete shells, which could provide catalytic pathways for oxidation/reduction reactions. Such reactions could eliminate combustion precursors and intermediates. On the other hand, it may be that transition metal compounds generate particulates within a fire, providing heterogeneous pathways for free-radical recombination. Whatever the mechanism, transition metal compounds appear to be highly effective.

Unfortunately, most transition metal compounds are either highly toxic (such as iron pentacarbonyl and chromyl chloride) or are solids, with no effective method for delivery and

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\*Linteris, G. T., and Gmurczyk, G., "Inhibition of Premixed Methane-Air Flames by Iron Pentacarbonyl," 15th International Colloquium on the Dynamics of Explosions and Reactive Systems, Boulder, Colorado 30 July - 4 August 1995. (Unpublished)

three-dimensional dispersion. However, one large group of transition metal compounds may have the properties needed for effective use as fire extinguishants and, at the same time, may have low toxicities. Organic ligands containing negative charges whose sum is equal to the positive charge on the central ion allow preparation of neutral transition metal compounds. Because the complexes are neutral, the compounds are nonionic, a property that gives two important characteristics: (1) Some neutral-charged complexes are known to have a relatively high volatility, a property that would help provide three-dimensional fire and explosion suppression. (2) All or nearly all of these compounds are soluble in organic liquids, providing a means for dispersion. Of particular interest are complexes containing fluorodiketone bidentate ligands, and synthesis and evaluation of these materials are now under way.

#### B. ENVIRONMENTAL CHARACTERISTICS

None of the transition metal compounds are expected to show any global environmental impact due to the metal itself. On the other hand, compounds of many of the transition metals are known to cause terrestrial environmental damage. Iron and possibly manganese are the two transition metals whose compounds are least likely to cause terrestrial environmental impacts.

#### C. TOXICITY

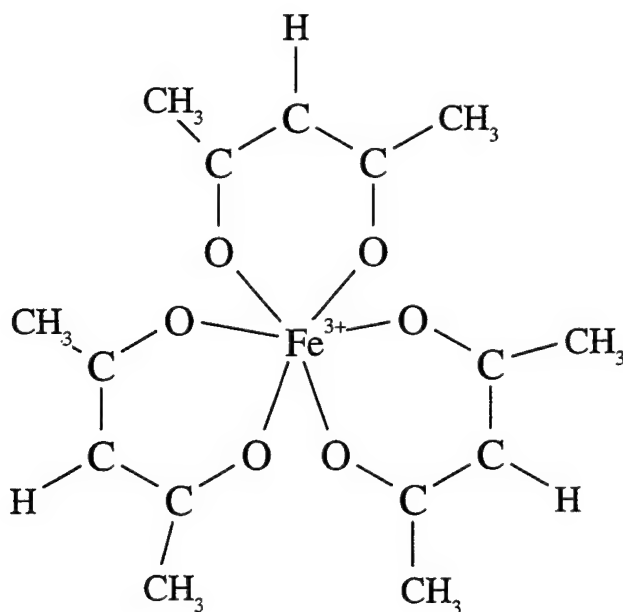
A number of iron compounds have a relatively low toxicity. Unfortunately, however, the highly volatile iron compounds known today are likely to be highly toxic. Iron pentacarbonyl is a lung irritant, has CNS effects, and causes damage to kidneys and liver (Reference 82). Many manganese compounds also have low toxicities. Again, however, the highly volatile manganese compounds such as the organometallics (those containing metal to carbon bonds) are likely to be toxic.

#### D. CANDIDATES

To a large extent, the chemistry of metal compounds is the chemistry of coordination compounds. Moreover, careful selection of appropriate ligands may allow the preparation of compounds with appropriate physical and toxicological properties.

## 1. 2,4-Pentanedionate(-1) (Acetylacetonate) Complexes

Many complexes are known for the 2,4-pentanedionate(-1) (acetylacetonate, "acac,"  $\text{CH}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3^-$ ) bidentate ligand, and most of these are uncharged. For example, ferric ( $\text{Fe}^{3+}$ ) ion forms the neutral compound tris[2,4-pentanedionato(-1)]iron(III) complex (XXV). Such acetylacetonate compounds, even though solids, have a significant vapor pressure and are often soluble in nonaqueous solvents. The fluorination of the ligand gives the 1,1,1-trifluoro-2,4-pentanedionate(-1) (trifluoroacetylacetonate, "tfac,"  $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CH}_3^-$ ) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (-1) (hexafluoroacetylacetonate, "hfac,"  $\text{CF}_3\text{C}(\text{O})\text{CHC}(\text{O})\text{CF}_3^-$ ) bidentate ligands, which form complexes with even higher vapor pressures.



XXV

## 2. Crown Ethers

Crown ethers (Reference 175) comprise another group of ligands that could prove appropriate for preparation of metal complexes as candidates for halon substitutes. Such complexes are known to be highly soluble in fluoroorganic solvents such as hydrofluoroethers (HFEs) (Reference 176) and hydrofluorocarbons (HFCs) (Reference 177). HFE and HFC

carriers combined with crown ether metal complexes could provide excellent fire extinguishment. It must be realized that even though economics and physical properties may prohibit the use of large concentrations of complexes in the carriers, the exceedingly great inhibition potential of metal compounds may allow outstanding performance even in the absence of large concentrations.

### 3. Manganese Compounds

Methylcyclopentadienyl manganese tricarbonyl (MMT) is a fuel additive that Ethyl corporation and/or Albemarle (a spin-off of Ethyl) have developed. Since a number of fuel additives appear to have fire extinguishment effectiveness, manganese compounds may provide fire extinguishment capabilities. Despite some concern, the EPA has allowed the use of MMT as a fuel additive.

It may be that MMT is too flammable for use and that fluorinated derivatives are needed. Among the fluorinated compounds possible are pentacarbonyl(trifluoromethyl)manganese(I)  $[\text{Mn}(\text{CF}_3)(\text{CO})_5]$ , pentacarbonyl(pentafluoroethyl)manganese(I)  $[\text{Mn}(\text{CF}_2\text{CF}_3)(\text{CO})_5]$ , pentacarbonyl[tetrafluoro-1-(trifluoromethyl)ethyl]manganese(I)  $[\text{Mn}(\text{CF}(\text{CF}_3)\text{CF}_3)(\text{CO})_5]$ , and pentacarbonyl(heptafluoropropyl)manganese(I)  $[\text{Mn}(\text{CF}_2\text{CF}_2\text{CF}_3)(\text{CO})_5]$  (Reference 178). It must be recognized that carbonyl derivatives are likely to have toxicity problems; however, these materials could provide starting points for additional concepts.

## E. CONCLUSIONS AND RECOMMENDATIONS

Transition metal compounds could provide "super" agents; however, it is likely that extensive research will be needed to find suitable compounds, if this is even possible. Nevertheless, a longer-term research program in this area could provide a large payback in view of the high effectiveness of some transition metal compounds as fire suppressants.

## SECTION XIV

### CONCLUSIONS

The purpose of this first phase of the project was to answer four questions: (1) What mechanisms are available for chemical action agents (CAAs) for protection against fires and explosions? (2) Based on these mechanisms, what families of chemicals could provide an advanced replacement for Halon 1301? (3) What is the preliminary assessment of manufacturability, global environmental impact, and toxicity for these families? (4) Taking all of the above into account, what are the prospects for a halon replacement for a total flood explosion and fire protection of normally inhabited areas that would allow use without major hardware changes?

The only chemical mechanism absolutely identified for flame extinguishment is removal of flame free radicals. This can occur through a reaction involving another chemical, as in the case of the bromine- and iodine-containing compounds, or through free radical recombination on surfaces. Note, however, that some compounds such as transition metal complexes and phosphorus-containing compounds, both of which in some cases exhibit high flame extinguishment activity, may offer a yet-unidentified mechanism for fire suppression.

Non-halocarbon compounds in the phosphorus, silicon, and transition metal families offer promise as candidates for streaming applications (Halon 1211 substitutes) and, to a lesser extent, as total-flood candidates (Halon 1301 replacements). Boron and sulfur compounds could also provide materials for investigation as halon substitutes. The tropodegradable halocarbons, on the other hand, offer significant promise as total-flood agents.

The non-halocarbon agents and the tropodegradable halocarbons both hold high promise as environmentally acceptable halon substitutes. The tropodegradable halocarbons, however, are the easiest to manufacture and, due to the large amount of available toxicity information, will be the easiest materials among those considered here for which to address toxicity concerns.

Among the agents examined in this report, only the tropodegradable halocarbons offer significant promise as Halon 1301 replacements with minimal retrofit in the near term.

## A. TROPODEGRADABLE HALOCARBONS

Tropodegradable replacements are halocarbons with very low atmospheric lifetimes. In most cases, this provides near-zero global warming and ozone depletion. There are two caveats. We designate all compounds that are rapidly removed from the troposphere as "tropodegradable," whether or not the removal actually involves molecular destruction. We also apply the term "tropodegradable" only to compounds that are removed rapidly. For this reason such materials as HCFCs and HFCs break down in the atmosphere relatively inefficiently, and these compounds are not considered tropodegradable. No sharp dividing line between rapid and non-rapid tropospheric degradation has been set; however, we generally designate chemicals with atmospheric lifetimes of days to weeks as being tropodegradable.

Owing to their short atmospheric lifetimes, tropodegradable compounds have decreased global environmental impacts—global warming, potential for ozone depletion, and atmospheric persistence. Increasing pressure for regulatory action to address global warming makes the tropodegradable compounds of particular promise. In the past, the U.S. has not been considered supportive of limitations on greenhouse gas emissions, and will not meet the voluntary goal of reducing emissions to 1990 levels by the year 2000, as established by the 1992 Rio de Janeiro climate-change treaty. Now, however, the U.S. has changed position. At the 2nd Conference of the Parties to the Framework Convention on Climate Change (COP2), in Geneva, Switzerland in July 1996, the U.S. representative announced that the U.S. will seek legally binding limits on emissions of gases that could cause global warming (Reference 179). At COP2, the strongly worded Geneva Declaration was adopted by a majority of the Parties. The Declaration instructs Parties "to accelerate negotiations on the text of a legally binding protocol or another legal instrument to be completed in due time for adoption at the third session of the Conference of the Parties," which is scheduled for 1-12 December 1997 in Kyoto, Japan (Reference 180).

At least six mechanisms are available to reduce the atmospheric lifetimes of molecules: (1) reaction with hydroxyl free radicals (OH), (2) reaction with tropospheric ozone (O<sub>3</sub>), (3) photodecomposition, (4) rainout, (5) thermal decomposition, or (6) hydrolysis due to atmospheric moisture (Reference 181). Hydrolysis is generally unimportant here, however, since



compounds that hydrolyze rapidly (e.g., compounds with halides) are usually toxic. For effective chemical suppression by halocarbons, bromine (or iodine) should be present. Tropodegradable bromocarbons and iodocarbons may give global environmental acceptability even though they contain potent ozone depleting elements.

TABLE 18. MECHANISMS FOR TROPOSPHERIC REMOVAL.

Primary removal mechanisms	Example families
Reaction with atmospheric hydroxyl	Alkenes, aromatics, hydrogen-containing amines, hydrogen-containing ethers, carbonyls
Reaction with tropospheric ozone	Alkenes
Photodegradation	Iodides, carbonyls, bromides
Physical removal (primarily, rainout)	Polar substituted compounds (carbonyl compounds, alcohols, amines, and, possibly, some ethers)
Thermal decomposition	<sup>a</sup> Highly reactive materials
Hydrolysis	<sup>a</sup> Compounds with halogens directly bonded to phosphorus, silicon, and metals

<sup>a</sup>Of little or no interest as halon replacement candidates due to toxicity and stability concerns.

The tropodegradable compounds of primary interest are iodocarbons, hydrobromofluoroethers (HBFE), hydrobromofluoroamines (HBFA), fluorobromo unsaturated compounds (alkenes and aromatics), and bromofluorocarbonyl compounds. Most of the materials are highly fluorinated (to decrease flammability and hepatotoxicity), but in many cases are not completely fluorinated. These materials appear to have very short atmospheric lifetimes, on the order of days or weeks. Thus the Ozone Depletion Potentials (ODPs) and Global Warming Potentials (GWPs) are near zero. The major problem is toxicity. The only iodocarbon having a reasonable toxicity identified to date is trifluoromethyl iodide (CF<sub>3</sub>I), and even this material has too high a toxicity to be considered for total-flood applications in normally occupied areas. Other iodocarbons appear to be more toxic. Note, however, that no information is available on aromatic iodides and these materials may have acceptable toxicities.

## B. NON-HALOCARBONS

The most promising non-halocarbon compounds are the phosphorus compounds (particularly phosphorus nitrides), bromine-substituted silicon and siloxane compounds, and transition metal compounds. A number of these non-halocarbon materials are solids or high boiling point liquids; however, many of these appear to have vapor pressures sufficiently high such that they could volatilize completely. Carriers such as hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) may be necessary in some cases. Of particular interest are the phosphorus nitrides. Preliminary work on these materials shows them to have extinguishment concentrations much less than those of the halons.

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## APPENDIX A

### GLOSSARY

**Aliphatic**—Straight-chain, branched-chain, or cyclic hydrocarbon structures containing carbon atoms linked by single  $sp^3$ - $sp^3$  bonds.

**Alkane**—A saturated hydrocarbon with the general formula  $C_nH_{2n+2}$  (e.g., butane,  $CH_3CH_2CH_2CH_3$ ) and derivatives thereof.

**Alkene**—A hydrocarbon containing one or more carbon-carbon double bonds or derivatives thereof. Hydrocarbons with a single double bond have the general formula  $C_nH_{2n}$  (e.g., 1-butene,  $CH_2=CHCH_2CH_3$ ).

**Alkoxy**—A group of the type -OR, where R is an aliphatic hydrocarbon radical or a substituted aliphatic radical. Examples are methoxy ( $-OCH_3$ ) and ethoxy ( $-OC_2H_5$ ).

**Alkyl**—An aliphatic substituent. Examples are methyl ( $-CH_3$ ), ethyl ( $-CH_2CH_3$  or  $-C_2H_5$ ), *n*-propyl ( $-CH_2CH_2CH_3$  or  $-C_3H_7$ ), *i*-propyl [ $-CH(CH_3)_2$ ], *n*-butyl ( $-CH_2CH_2CH_2CH_3$  or  $-C_4H_9$ ), *t*-butyl [ $-C(CH_3)_3$ ].

**Allyl**—The  $-CH_2-CH=CH_2$  group.

**Antagonism**—An effect wherein a mixture shows an activity less than would be predicted from the activities of the components. Antagonism can be observed in fire suppression performance, toxicity, and other characteristics.

**Aromatic**—Cyclic molecules or fused cyclic molecules containing formally alternating single and double bonds with delocalized  $\pi$  electrons. The most common simple aromatic compound is benzene.

**Aryl**—Aromatic substituents derived from benzene and related compounds. Examples are phenyl ( $-C_6H_5$ ), tolyl ( $-C_6H_4CH_3$ ), and naphthyl ( $-C_{10}H_7$ ).

**Aryloxy**—A group of the type -OR, where R is an aryl group. Examples are phenoxy ( $-OC_6H_5$ ) and naphthoxy ( $-OC_{10}H_7$ ).

**Covalent**—Bonding in which electrons are shared by two atoms, both of which contribute to the bonding pair(s).

**Cyclic**—Arranged in a closed ring rather than an open chain.

**Cycloaliphatic**—Cyclic aliphatic molecules such as cyclohexane,  $C_6H_{12}$ .

**Dimer**—A molecule consisting of two identical joined units. An example is diborane,  $B_2H_6$ , which is composed of two  $-BH_3$ - groups.

**Dimerization**—Formation of a dimer.

**Disilane**—The compound  $\text{Si}_2\text{H}_6$  or derivatives thereof.

**Dissociation**—The separation of a molecule into atomic or ionic fragments when exposed to heat, electric energy, or a solvent.

**Edema**—Accumulation of fluid, often in lungs.

**Endothermic**—A term applied to any process during which heat is absorbed.

**Ester**—A compound formed from an alcohol and an oxyacid by elimination of water. This includes compounds containing the groups  $-\text{BOR}$ ,  $-\text{P}(\text{O})\text{OR}$ ,  $-\text{C}(\text{O})\text{OR}$ , and  $-\text{SiOR}$ , where R is an organic group.

**Ethyl**—The  $-\text{C}_2\text{H}_5$  group, second of the homologous series of saturated aliphatic radicals of the type  $\text{C}_n\text{H}_{2n+1}$ .

**Exothermic**—A term applied to any process during which heat is released.

**Ground State**—The lowest energy quantum mechanical state of an atom or a molecule. In this report, this is usually the lowest energy electronic state.

**Haloalkane**—Saturated halocarbons containing only carbon, halogen, and, in some cases, hydrogen atoms.

**Halocarbon**—A compound of carbon and one or more halogen atoms with or without hydrogen.

**Halide**—A compound a halogen atom. Alternatively, a negative ion of one of the halogen atoms (e.g., fluoride,  $\text{F}^-$ ; chloride,  $\text{Cl}^-$ ; bromide,  $\text{Br}^-$ ; or iodide,  $\text{I}^-$ ).

**Haloalkyl**—An aliphatic substituent containing one or more halogen atoms. Examples are tribromomethyl ( $-\text{CBr}_3$ ) and 2-chloroethyl ( $-\text{CH}_2\text{CH}_2\text{Cl}$ ).

**Halogen**—One of the elements or atoms fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The last element is radioactive and is not considered in this project.

**Homolog**—A compound forming part of a homologous series, and hence closely related to the other compounds in that series in structure, composition, and physical properties.

**Homologous**—An adjective used to describe homologs.

**Hydride**—A binary compound of hydrogen with some other element.

**Hydrocarbon**—A binary compound of carbon and hydrogen. This term includes aliphatic compounds (paraffins), compounds containing double bonds (olefins), and aromatics.

**Hydrochlorofluorocarbon**—An aliphatic compound containing only hydrogen, fluorine, chlorine, and carbon. An example is HCFC-123,  $\text{CHCl}_2\text{CF}_3$ .

**Hydrofluorocarbon**—An aliphatic compound containing only hydrogen, fluorine, and carbon. An example is HFC-134a,  $\text{CH}_2\text{FCF}_3$ .

**Hydrolysis**—The reaction of a material with water. Here, this usually refers to the reaction of a halide with water to form a hydrogen halide, e.g.,  $\text{RX} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{HX}$ , where X is a halogen atom and R is any group.

**Hydroxyl**—The -OH group, common to alcohols, ROH, and water or the unattached  $\bullet\text{OH}$  free radical.

**Hyperplasia**—Abnormal increase in tissue cells.

**Iso**—Here, an adjective designating a 3-carbon alkyl group attached at the middle carbon atom. The isopropyl group (also designated as the *i*-propyl group) is  $-\text{CH}(\text{CH}_3)_2$ .

**Macrophage**—Large phagocyte (cell engulfing foreign material).

**Methyl**—The  $-\text{CH}_3$  group, simplest member of the homologous series of saturated aliphatic radicals of the type  $\text{C}_n\text{H}_{2n+1}$ .

**Monomer**—A single molecular unit, usually a building block for a polymer.

**Monosilane**—The compound  $\text{SiH}_4$  or derivatives thereof.

**Normal**—An adjective designating a group comprised of a straight chain. For example, the normal-butyl group (usually designated as an *n*-butyl group) is  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ .

**Olefin**—An unsaturated hydrocarbon containing one or more double bonds, an alkene. An example is ethene (ethylene),  $\text{H}_2\text{C}=\text{CH}_2$ .

**Oxidation**—The removal of electrons from an atom or ion making its charge more positive or less negative. In a more restricted sense, chemical combination with oxygen. Oxidation is also used as an adjective to describe the formal contribution of electrons to a bond as in oxidation state or oxidation number.

**Perfluorocarbon**—An aliphatic compound containing only fluorine and carbon. An example is FC-218 (sometimes called PFC-218),  $\text{CF}_3\text{CF}_2\text{CF}_3$ .

**Phenyl**—The cyclic  $-\text{C}_6\text{H}_5$  group derived from benzene.

**Phosphorus Nitride**—A compound containing phosphorus and nitrogen including such families as phosphazenes, phosphonitriles, and phosphazanes.

**Pi ( $\pi$ ) Bonding**—Bonding involving “sideways” overlap of atomic orbitals as opposed to sigma ( $\sigma$ ) bonding.

**Polymer**—A chemical compound in which some relatively simple unit structure or group is repeated throughout the molecules.

**Porphyrinuria**—Presence of porphyrin in urea.

**Propyl**—The  $-C_3H_7$  group, third in the homologous series of saturated aliphatic radicals of the type  $C_nH_{2n+1}$ .

**Resin**—A (usually) organic material that is characterized by being amorphous, isotropic, or plastic.

**Saturated**—Chemically combined to the extent allowed by the most commonly exhibited valence. Containing no double or triple bonds.

**Sigma ( $\sigma$ ) Bonding**—Bonding involving direct, end-on overlap of atomic orbitals.

**Silane**—Hydrides of silicon of the type  $Si_nH_{2n+2}$  or derivatives thereof.

**Silicate**—Inorganic silicates are minerals containing silicon, oxygen, one or more metals, and, sometimes, hydrogen. Occasionally, some organic compounds are referred to as silicates to denote their relationship to the hypothetical compound,  $Si(OH)_4$ .

**Siloxane**—A compound of silicon containing alternating silicon and oxygen atoms, sometimes called silicones. Examples are disiloxane,  $H_3Si-O-SiH_3$ , trisiloxane,  $H_3Si-O-SiH_2-O-SiH_3$ , etc.

**Singlet State**—An electronic state of an atom or a molecule in which there are no unpaired electrons.

**Synergism**—An effect wherein a mixture shows an activity greater than would be predicted from the activities of the components. Synergism can be observed in fire suppression performance, toxicity, and other characteristics.

**Synergist**—A chemical that enhances the activity of another chemical. In the case of flame retardants, a chemical that enhances the flame suppression of a retardant.

**Tertiary**—An adjective designating a 4-carbon alkyl group containing one carbon attached to three others. The tertiary butyl group (also designated as the *t*-butyl or *tert*-butyl group) is  $-C(CH_3)_3$ .

**Tetramer**—A molecule consisting of four identical joined units. An example is octafluorocyclotetraphosphazene,  $P_4N_4F_8$ , which is composed of four  $-PF_2N-$  groups.

**Transition State**—The intermediate state or the intermediate short-lived species that exists momentarily when reactants form products in a chemical reaction.

**Trifluoromethyl**—The  $-\text{CF}_3$  group, derived from the methyl group,  $-\text{CH}_3$ , by substitution with fluorine.

**Trimer**—A molecule consisting of three identical joined units. An example is hexafluorocyclo-triposphazene,  $\text{P}_3\text{N}_3\text{F}_6$ , which is composed of three  $-\text{PF}_2\text{N}-$  groups.

**Triplet State**—An electronic state of an atom or a molecule in which there are two unpaired electrons giving a resultant spin state of 1.

**Tropodegradable**—An adjective applied to compounds that are rapidly removed from the earth's troposphere by such mechanisms as photolysis, reaction with hydroxyl free radical, rainout, and physical removal.

**Unsaturated**—Containing one or more double or triple bonds. Also used to denote that further bonding is possible for one or more of the elements present in a compound.

**Valence**—A whole number that gives the combining power of an element with other elements. For covalent compounds, the valence is the number of bonds, with a double bond counting as two and a triple bond counting as three, that an atom can form with other atoms. For example, in  $\text{CH}_4$  and  $\text{O}=\text{C}=\text{O}$ , carbon has a valence of four (it is said to be tetravalent). This is the only valence observed for carbon except in some very rare solid state metal compounds and unstable, short-lived gaseous species.

**Vinyl**—The  $-\text{CH}=\text{CH}_2$  group.